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A SEMI-CLASSICAL THEORY OF MOLECULAR COLLISIONS[*]

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ABSTRACT

This research represents the first phase of a new attack on
the difficult problem of predicting the results of a collision
between polyatomic molecules. We treat the translational motion
of the molecules by classical mechanics, and the internal motions
by quantum mechanics. The effect on the trajectory of a quantum
transition of the internal coordinates is obtained by requiring that
the classical conservation laws of energy and angular momentum
be satisfied at all times. This method gives a description of the
molecular trajectories in both adiabatic and non adiabatic
collisions which is much more detailed than has been considered
previously. Such detailed information about the trajectories is
especially important for applications to the kinetic theory of gases.

Our theory requires that one know the relative probability
that a quantum transition of the internal coordinates takes place
at various points along the collision trajectory. Because of
diffraction effects and limitations due to the uncertainty principle,
such information is not directly available from quantum mechanics.

An approximate formula, suggested by the form of the quantum
mechanical equations, is proposed for calculating this probability
distribution.

The theory is illustrated by sample calculations for the exchange
of rotational energy between linear polar molecules. On the basis
of some of these calculations and some earlier work by F. J. Krieger
[Proj. RAND Report, RM-646 (1951)] a method is proposed for
calculating the viscosity of polar gases. The gas is viewed as a
mixture of molecular species, with each set of internal quantum
numbers defining a separate species. In non resonant collisions be-
tween linear molecules, the interaction energy is taken to be of the
form of the Lennard-Jones potential, with a repulsive energy term
proportional to the minus twelfth power of the separation and an at-
tractive term proportional to the minus sixth power of the separation.
When the molecules are in resonance, an additional term proportional
to the minus third power of the separation must be included. This
term may be either repulsive or attractive; its coefficient can be
calculated from a knowledge of the internal quantum numbers.
In order to test this proposed method for predicting the viscosity
of polar gases it would be necessary to calculate the dynamics of
collisions governed by the resonant potential in which the term in
the cube of the separation corresponds to a repulsive force. Calcu-
lations for the Lennard-Jones potential and for the resonant potential
in which the cubic term corresponds to an attractive force are
already in existence.

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I. BACKGROUND FOR THE STUDY OF INELASTIC MOLECULAR COLLISIONS

1.1 Introduction

The kinetic theory of dilute gases, as developed by Boltzmann, Enskog, Chapman[1], and others, is valid only for the case of monatomic gases, since the potential energy of interaction between two molecules is assumed to depend only on the distance of separation. The theory of transport phenomena in gases made up of molecules with internal degrees of freedom has recently been developed by Wang Chang and Uhlenbeck[2], and by J. de Boer[3].

Whereas the transport coefficients in the Enskog theory may be calculated from a knowledge of the angle of deflection in a bimolecular collision, the theory for polyatomic molecules requires knowledge of the full set of differential scattering cross sections corresponding to all possible quantum transitions of the internal degrees of freedom.

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1. The classic text on the subject is: S. Chapman and T. G.
    Cowling, The Mathematical Theory of Non Uniform Gases,
    Cambridge University Press, 1939.
    A more recent text of wider scope which gives up to date
    developments in the field and emphasizes the practical
    application of the theory is: J. O. Hirschfelder, C. F. Curtiss,
    and R. B. Bird, The Molecular Theory of Gases and Liquids,
    Wiley, 1954. This reference will be quoted frequently with
    page references, and will be abbreviated MTGL.

2. C. S. Wang Chang and G. C. Uhlenbeck, Univ. of Michigan,
    publication CM-681 (1951).

3. Unpublished, See MTGL. p. 501.

Unfortunately, it has not been possible to evaluate these differential scattering cross sections for a single case, because of the complexity of the quantum mechanical description of a thermal collision between molecular systems. The work reported in this thesis is directed toward an evaluation of these differential scattering cross sections by means of a semi-classical description of the collision process.

The semi-classical formulation of the collision problem depends on the assumption that the relative translational motion of the colliding molecules may be described by classical mechanics, while the internal motions - electronic, vibrational, and rotational - are described by quantum mechanics. This method, sometimes called the method of impact parameters, has frequently been applied to collision problems in which it was desired to determine only the total probability of an internal transition, and in which the classical trajectories could be approximated by straight lines along which the molecules moved at constant velocity.

In this research we describe an extension of the semi-classical method which gives the detailed information about the trajectories, which, together with the probability of internal transitions, is necessary for evaluation of the differential scattering cross sections. The extension depends on the assumption that the collision is nearly adiabatic, so that the Schroedinger equation describing the internal motions may be solved for every intermolecular separation with that quantity appearing only as a parameter in the wave functions and energies of the solutions.

The energy term so calculated, depending on the intermolecular separation and internal quantum states, is taken as the effective potential energy of interaction from which the classical trajectories may be calculated by integration of the equations of motion. In

principle this integration can always be carried out, though in most cases it will be necessary to resort to numerical methods. The "elastic" trajectories so calculated describe the motion of the molecules as long as the internal quantum state does not change. They include the important distortion effect of the intermolecular potential on the incoming and outgoing trajectories which has been ignored in most previous semi-classical calculations and which is ignored in the Born approximation of quantum mechanical scattering theory.

Since the relative position of the colliding molecules is given precisely as a function of time by these elastic trajectories, the method of time dependent perturbations may be used to calculate the probability that a quantum mechanical transition of internal coordinates occurs during an encounter. When a transition does occur, it is assumed to take place instantaneously, so that the direction and velocity of the molecular motions change abruptly in accordance with the classical conservation laws of energy and angular momentum. The trajectories after such a transition are segments of other elastic trajectories characteristic of the intermolecular potential determined by the new internal quantum states, and with boundary conditions determined from the conservation laws. A given internal transition can thus lead to a whole family of inelastic trajectories, depending where along the trajectory the quantum transition takes place. An approximate expression, suggestion by the time dependent perturbation formulae, is given which describes the relative probability of transition along the trajectory. This expression is modified in special cases by a set of "selection rules" resulting from the fact that for a given transition there are points along the trajectory at which the conservation laws cannot be satisfied.

The semi- classical formulation of the collision problem has several advantages over the quantum mechanical scattering formula-

tion: It is not necessary to assume that the energy exchange in an inelastic collision is small, so that, for example, the method would be expected to be applicable to a study of rotational energy transfer in collisions between hydrogen molecules. The description of the relative translational motion of the molecules, which leads to the greatest difficulties in the quantum mechanical approach through an infinite set of coupled radial equations, can in principle always be given in the semi-classical formulation by direct integration of the Newtonian equations of motion. Finally, the semi-classical formulation naturally falls into several distinct steps each with clear physical significance, so that the significance and effects of various simplifying approximations are perhaps more readily seen than in the quantum mechanical method.

Following a general presentation of the semi-classical theory of inelastic collisions, we give a detailed description of the theory for the case of the transfer of rotational energy in collisions between rigid, linear molecules containing ideal electric dipoles. This model is of particular interest in kinetic theory since the high degree of asymmetry in the intermolecular potential would seem to make application of the Enskog theory for spherical molecules inappropriate, even as a first approximation. We include sample calculations of the effective intermolecular potential and probability of transition along the trajectory for typical cases. These sample calculations are of value for indicating simplifications which might be made in an approximate evaluation of the differential scattering cross sections. The details of a sample inelastic trajectory indicate the importance of the inelastic transfer on the trajectory.

The effective intermolecular potential arising from the adiabatic interaction of such rotating linear dipoles has been calculated for several typical cases from well known formulae due to F. London.

When the principle rotational quantum numbers of the colliding mole-
cules differ by one - the case of resonance interaction - long range
attractive and repulsive potentials arise. With the help of the semi-
classical theory it is shown why the Enskog theory actually is able
to predict the coefficient of viscosity of polar molecules when a poten-
tial energy function is used which includes the long range interactions.

The dependence of the rotational transition probability on rela-
tive velocity, impact parameter, and magnitude of the energy transfer
is calculated for some sample cases. Since the transition probability
varies rapidly as these variables are changed, it is seen that the
important contributions to the cross sections would be expected to
come from collisions characterized by rather narrow ranges of these
variables.

Calculations of the relative probability that transitions occur
at various points along a trajectory indicate that the distance of closest
approach of the molecules, frequently taken as the most probable
place for a transition, may actually be a very unlikely place. Instead,
the regions where the effective intermolecular potential is changing
most rapidly with time are indicated as the most likely points for a
transition. This fact, too, would be of great value for approximate
calculations of the cross sections.

The special case of the transition probability when the mole-
cules undergo a resonant transition is discussed. As long as the
molecules interact strongly enough to give an angle of deflection appre-
ciably different from zero, it is shown that the classical analogue of
the transition probability corresponds to a frequent exchange of the
quantum of rotational energy during the collision. Thus when the
molecules finally separate after the encounter there is equal probabil-
ity that either one of them will have the extra quantum of rotational
energy.

This detailed consideration of rotational transitions in polar molecules is followed by a brief discussion of the form the theory would take in the consideration of vibrational and electronic transitions.

1.2 Inelastic Collisions and the Kinetic Theory of Gases

The kinetic theory of gases composed of particles which interact according to a spherically symmetric interaction potential is completely understood[1]. That is, the transport coefficients of a monatomic gas[4] may be calculated to any degree of accuracy for an arbitrary intermolecular potential. The derivation begins with the Boltzmann equation[5] which specifies the singlet distribution of molecules in phase space. Solutions of this equation due to Enskog

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4.   Actually the theory may be used satisfactorily to predict the transport coefficients except thermal conductivity, for molecules like O_2 and N_2 which are nearly spherical.

5.   MTGL p. 444.

and Grad lead, finally, to the formulae for calculation of the transport coefficients. The dynamical information required for these calculations is simply the angle of deflection in a bimolecular collision χ as a function of the collision parameter b and the relative velocity g. (See Fig. 2.1).
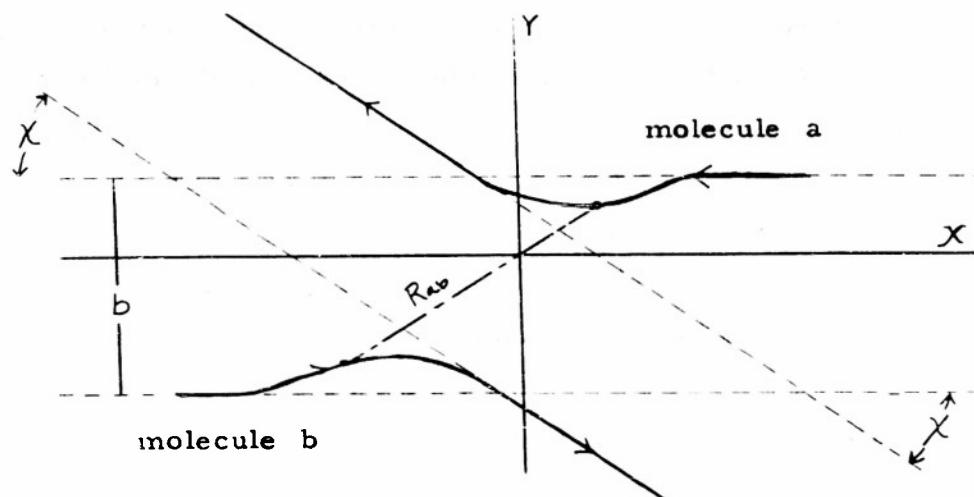
Fig. 2.1   A Typical Bimolecular Collision Pictured in a Coordinate System Translating with the Center of Mass of the System.

The classical Boltzmann equation does not apply if the molecules have internal degrees of freedom. By assuming that the internal degrees of freedom could be treated quantum mechanically while the translational motion was treated with classical mechanics, Wang Chang and Uhlenbeck were able to modify the theory so that it would describe this more complicated situation. In principle, their method amounts to considering the gas as a mixture, with each set of internal quantum states defining a separate species. A separate Boltzmann equation gives the distribution function for each species, and the

equations are coupled in the sense that collisions tranrfer molecules from one species to the other. A solution of these coupled equations, similar to Enskog's, then leads to the expressions for the transport coefficients. Wang Chang and Uhlenbeck give the formulae for the transport coefficients for the two limiting cases of very easy and very difficult exchange of internal energy. Whereas the theory for spherical molecules depended only on the angle of deflection $\chi_{(b,g)}$, the theory for polyatomic molecules depends on the differential scattering cross sections, $I_{ij}^{\kappa\ell}(g,\chi,\psi)$. The differential cross section $I_{ij}^{\kappa\ell}(g,\chi,\psi)$ for a collision process is defined as the fraction of the molecules with relative velocity g which are scattered from a uniform incident beam of flux one molecule per unit area per unit time, into a unit solid angle in the direction χ, ψ while the internal quantum numbers specifying the system go from i and j to k and l.

Although we do not intend to describe either of these theories in any detail, it will be instructive to compare typical results from the two theories in order to see the effect of the internal degrees of freedom. For molecules with spherical potentials, the first approximation to the reciprocal of the viscosity coefficient is given by[6]

$$\frac{1}{[\eta]_1} = \frac{16\pi}{5\sqrt{\pi m kT}}\left(\frac{\mu}{2kT}\right)^8 \int_0^\infty \int_0^\infty \left\{g^4\left[1-\cos^2\chi_{(b,g)}\right]\right\} e^{-\frac{\mu g^2}{2kT}} g^3 \, b \, db \, dg \quad (1.2\text{-}1)$$

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6. MTGL p. 527

Here $[\eta]_1$ is the first approximation to the coefficient of viscosity, μ is the reduced mass, g the relative speed of the molecules, b the collision parameter, and $\chi_{(b,g)}$ is the angle of deflection of the collision. These quantities are best understood by reference to Fig 2.1 where a typical collision is pictured in a coordinate system translating with the center of mass.

The important thing to notice about Eq. 1.2-1 is that it amounts, essentially, to a calculation of the quantity $g^4[1 - \cos^2 \chi_{(b,g)}]$ averaged over all collisions. Since $2\pi b \, db$ is the probability that a collision in a dilute gas near equilibrium will occur with collision parameter between b and $b + db$, and since $g^3 e^{-\frac{\mu g^2}{2kT}}$ is proportional to the probability that the relative velocity of the encounter will lie between g and $g + dg$, the averaging corresponds to an equilibrium distribution of all possible collisions. The angle of deflection, $\chi_{(b,g)}$ depends only on b and g, so the average may be accomplished by a double integration over these two initial conditions.

When the molecules possess internal degrees of freedom, and when the energy of those degrees of freedom exchanges readily with the translational energy, Wang Chang and Uhlenbeck[7] show that the expression for the reciprocal of the coefficient of viscosity is given by

$$\frac{1}{[\eta]} = \frac{16\pi}{5\sqrt{\pi m kT}} \left(\frac{\mu}{2kT}\right)^{\delta} \sum_{\substack{i,j \\ \kappa,\ell}} \frac{e^{-(E_{\alpha}^i + E_b^j)}}{\left(\sum_s e^{-E_{\alpha}^s}\right)\left(\sum_s e^{-E_b^s}\right)} \int_0^{\infty} dg \int_0^{\pi} \sin\chi \, d\chi \int_c^{2\pi} d\psi$$

(1.2-2)

$$\left\{ g^4(1 - \cos^2\chi) + \frac{2}{3} g^2 \Delta E_{ij}^{\kappa\ell}\left(1 - \frac{3}{2}\sin^2\chi\right) \right\} I_{ij}^{\kappa\ell}(g, \chi, \psi) \, g^3 e^{-\frac{\mu g^2}{2kT}}$$

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7. Loc. cit. p. 20

Here E_a^i is the internal energy of molecule a when it is in the i'th quantum state, $\triangle E_{ij}^{\kappa\ell}$ is the net change in internal energy, and ψ is the azimuthal scattering angle which tells how far the final trajectory is bent out of the plane of the initial trajectories. The significance of χ is unchanged.

Equation 1.2-2 differs from Eq. 1.2-1 in two respects. The property of the collision which is to be averaged is now

$$\left\{ g^4 \sin^2\chi + \tfrac{2}{3} g^2 \triangle E_{ij}^{-\kappa\ell}\left(1 - \tfrac{3}{2}\sin^2\chi\right) \right\} \tag{1.2-3}$$

Clearly this reduced to the expression in Eq. 1.2-1 when the collision is elastic, since then $\triangle E_{ij}^{\kappa\ell}$ is zero. In the second place, we now label the encounters not with the initial conditions b and g, but with the initial velocity g and the final scattering angles χ and ψ, together with the initial and final internal quantum states. This change in point of view complicates the averaging process and necessitates introduction of the differential scattering cross sections

$I_{ij}^{\kappa\ell}(g, \chi, \psi)$. The quantity $I_{ij}^{\kappa\ell}(g, \chi, \psi) \sin\chi \, d\chi \, d\psi$ now plays a rule analogous to $2\pi b \, db$, enabling us to make an average over all possible encounters even though we are counting them with respect to labels characteristic of the final state[*]. Evaluation of these cross sections represents the chief problem in the application of the kinetic theory of polyatomic molecules. In the next section we describe the quantum mechanical significance and evaluation of the cross sections.

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[*] This change of variables could be carried out in the classical formula by changing from an integration over b to one over χ then $2\pi b \, db = 2\pi \left[\dfrac{b}{\sin\chi}\dfrac{db}{d\chi}\right]\sin\chi \, d\chi$.

The quantity in brackets is just what is usually defined as the classical differential scattering cross section. (See for example, H. Goldstein, Classical Mechanics, Addison Wessley, 1951). For the case of rigid spheres it is simply the geometric cross section πd^2 where d is the radius of the sphere.

1.3 The Quantum Theory of Scattering[8,9]

A detailed discussion of the quantum theory of scattering would be out of place here, but we shall outline enough of the theory to show the quantum mechanical significance of the cross section, and to indicate the chief approximate methods which have been applied to studies of molecular collisions. The approximate methods will be of use for purposes of comparison with their counterparts in the semi-classical theory to be presented in Chapters II and III.

Suppose we consider isolated molecules a and b, whose internal Hamiltonians are H_a and H_b and whose wave functions u_a^i and u_b^j and energy levels E_a^i and E_b^j

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8. Most of this section is based on material in W. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions Oxford Press, second ed. (1949).

9. For recent important developments in the fundamental theory of scattering, see :

   D. R. Bates, A. Fundaminsky, H. S. W. Massey, and J. W. Leech, Phil. Trans. Roy. Soc. A-860, 93, (1950).

   Breit, Rev. Mod. Phys. 23, 238 (1951)

   S. Altschuler Phys. Rev. 89, 1278 (1953); 95, 546 (1954)

   C. F. Curtiss, J.O. Hirschfelder and F. T. Adler J. Chem. Phys. 18, 1638 (1950)

   C. F.Curtiss, J. Chem. Phys. 21, 1199 (1953)

are obtained by solutions of the equations

$$[H_a(r_a) - E_a^i] \, u_a^i(r_a) = 0$$

$$[H_b(r_b) - E_b^j] \, u_b^j(r_b) = 0$$

Here r_a and r_b denote all of the coordinates necessary to specify the configurations of molecules a and b relative to their mass centers.

If $\underline{R}_{ab}$ is the position of molecule b relative to molecule a, g the relative velocity, μ the reduced mass, and $\Phi(R_{ab}, r_a, r_b)$ the potential energy of interaction, then the wave equation of the colliding system in relative coordinates is[10]

$$\left[\frac{\hbar^2}{2\mu} \nabla^2_{R_{ab}} - H_a(r_a) - H_b(r_b) + \frac{1}{2}\mu g^2 + E_a^i + E_b^j - \Phi(R_{ab}, r_a, r_b)\right] \Psi(R_{ab}, r_a, r_b) \quad (1.3-2)$$
$$= 0$$

The problem is to solve Eq. 1.3-2 with boundary conditions corresponding to a molecular collision. Let us look for the solution which describes the scattering of a uniform beam of molecules in state i from a molecule in state j. Taking the incident beam along the positive z axis, and neglecting symmetry effects, the solution may be expanded in the complete set of functions $u_a^\lambda(r_a) \, u_b^\mu(r_b)$ (including the continuum, for ionized states). Thus

$$\Psi^{ij}(R_{ab}, r_a, r_b) = \sum_{\lambda,\mu} F_{ij}^{\lambda\mu}(R_{ab}) \, u_a^\lambda(r_a) \, u_b^\mu(r_b) \qquad (1.3-3)$$

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10.   W.F. Mott and H.S.W. Massey, loc, cit. p. 140.

To satisfy the boundary conditions, we must have for large $|R_{ab}|$

$$F_{ij}^{ij} \sim e^{i K_{ij} z} \mu_a^i(r_a)\mu_b^j(r_b) + \frac{\sigma_{ij}^{ij}(\chi,\psi)}{|R_{ab}|} e^{i K_{ij}^{ij}|R_{ab}|} \qquad (1.3\text{-}4)$$

and

$$F_{ij}^{\lambda\mu} \sim \frac{\sigma_{ij}^{\lambda\mu}(\chi,\psi)}{|R_{ab}|} e^{i K_{ij}^{\lambda\mu}|R_{ab}|} \qquad \lambda,\mu \neq i,j$$

Here

$$K_{ij}^2 = \left(\frac{\mu g}{\hbar}\right)^2 \qquad K_{\lambda\mu}^2 = \frac{2\mu}{\hbar^2}\left[\tfrac{1}{2}\mu g^2 + E_a^i + E_b^j - E_a^\lambda - E_b^\mu\right]$$

It may be shown that[11]

$$I_{ij}^{\kappa\ell}(g,\chi,\psi) = \frac{K_{\kappa\ell}}{K_{ij}}\left|\sigma_{ij}^{\kappa\ell}(g,\chi,\psi)\right|^2 \qquad (1.3\text{-}5)$$

The radial functions $F_{ij}^{\ell m}(R_{ab})$ are given by the set of coupled equations

$$\left(\nabla^2 + K_{\ell m}^2\right)F_{ij}^{\ell m}(R_{ab}) = \frac{2\mu}{\hbar^2}\sum_{\lambda,\mu} F_{ij}^{\lambda\mu}(R_{ab})\, \Phi_{\lambda\mu,\ell m} \qquad (1.3\text{-}6)$$

where

$$\Phi_{\lambda\mu,\ell m} = \iint \mu_a^{\lambda*}(r_a)\,\mu_b^{\mu*}(r_b)\,\Phi(R_{ab},r_a,r_b)\,\mu_a^\ell(r_a)\,\mu_b^m(r_b)\,dr_a\,dr_b$$

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11. ibid. p. 137

Obtaining solutions to this infinite set of coupled radial equations constitutes the chief problem of the quantum mechanical method. As Zener has pointed out[12], it is the difficulty of handling the radial equations in the quantum mechanical method that suggests development of a semi-classical theory for investigating low velocity molecular collisions. The translational motion of molecules in thermal collisions is very nearly classical, so that one might hope for a considerable simplification when the problem is reformulated in such a way as to utilize Newtonian mechanics for a description of the relative molecular motion.

We shall now list three approximate solutions of the scattering equations which are of importance in the study of molecular collisions. One can, to some extent, attach a physical significance to the mathematical approximations made in each case.

a) The Born Approximation.

If on the right hand side of Eq. 1.3-6 we take

$$F_{ij}^{ij}(\underline{R}_{ab}) = e^{i[K_{ij}\,\underline{n}_0 \cdot \underline{R}_{ab}]}$$

$$(1.3-7)$$

$$F_{ij}^{lm}(\underline{R}_{ab}) = 0 \qquad l, m \neq i, j$$

where $\underline{n}_0$ is a unit vector in the direction of the incident beam and $\underline{n}$ is a unit vector in the direction of χ, ψ then it may be shown[13] that

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12. C. Zener, Phys. Rev. **37**, 557 (1931)

13. W. F. Mott, and H. S. W. Massey, loc. cit. p. 143.

$$I_{ij}^{\kappa\ell}(g,\chi,\psi) = \frac{\mu^{2}}{h^{4}} \frac{K_{\kappa\ell}}{K_{ij}} \left| \int e^{i[K_{ij}\underline{m}_{e} - K_{\kappa\ell}\underline{m}]\cdot \underline{R}_{ab}} \overline{\Phi}_{ij,\kappa\ell} d\tau \right|^{\nu} \tag{1.3-8}$$

To this approximation, the distortion of the incoming and
outgoing waves by the interaction potential is minimized, since
they are taken to be plane waves. In a semi-classical treatment
this would correspond to taking these trajectories as straight lines
along which the molecules travelled at constant velocities character-
istic of the initial and final translational energy. Thus the method
is best suited to a study of high energy collisions where the trans-
lational motion is only slightly perturbed by the collision. Because
of the relative simplicity of the method, however, Kerner[14] has
used it for a study of both vibrational and rotational energy transfer
in thermal molecular collisions.

b) Distorted waves.

If we make the less drastic assumption that the non diagonal
matrix elements on the right hand side of Eq. 1.3-6 are so small
that we may neglect all terms except the diagonal ones:

$$\Phi_{\ell m, \ell m} F_{ij}^{\ell m}(\underline{R}_{ab})$$

and the off diagonal ones connected with the incident state:

$$\Phi_{ij, \ell m} F_{ij}^{ij}(\underline{R}_{ab})$$

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14.   E. H. Kerner, Phys. Rev. 92, 899 (1953 and 91,
       1174, (1953).

then it **may** be **shown**[15] that

$$I_{cj}^{\kappa\ell}(\vartheta,\chi,\psi) = \frac{\mu^2}{\hbar^4}\frac{K_{\kappa\ell}}{K_{cj}}\left|\int F_{cj}^{cj}(R_{ab})\,\mathcal{F}_{cj}^{-\kappa\ell}(R_{ab})\,\Phi_{cj,\kappa\ell}\,d\tau\right|^2 \tag{1.3-9}$$

Here $\quad F_{cj}^{cj}(\underline{R}_{ab})\quad$ is the solution of

$$\left[\nabla^2 + K_{cj}^2 - \frac{2\mu}{\hbar^2}\Phi_{cj,cj}\right]F_{cj}^{cj}(R_{ab}) = 0 \tag{1.3-10}$$

and the $\quad \mathcal{F}_{cj}^{\kappa\ell}(\underline{R}_{ab})\quad$ are solutions of

$$\tag{1.3-11}$$
$$\left[\nabla^2 + K_{\kappa\ell}^2 - \frac{2\mu}{\hbar^2}\Phi_{\kappa\ell,\kappa\ell}\right]\mathcal{F}_{cj}^{\kappa\ell}(\underline{R}_{ab}) = 0$$

In this approximation some of the distortion of the incident and outgoing waves by the scattering field is taken into account. Instead of using plane waves for the incident and scattered waves, we now

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15.   W. F. Mott and H. S. W. Massey, loc. cit. p. 146.

have waves distorted by the diagonal elements of the interaction potential. This is the method most frequently used for the investigation of molecular collisions.[16-22]

c) Perturbed stationary states.

In this method the original derivation is varied slightly. It is assumed that the encounter is nearly adiabatic, and that for every intermolecular distance $\underline{R}_{ab}$ the equation

$$\left[H_a(\underline{r}_a) + H_b(\underline{r}_b) + \Phi(\underline{r}_a, \underline{r}_b, \underline{R}_{ab}) - E(\underline{R}_{ab}) \right] \psi_{(\underline{r}_a, \underline{r}_b \mid \underline{R}_{ab})}^{ij} = 0 \qquad (1.3-12)$$

has been solved. The $\psi^{ij}(\underline{r}_a, \underline{r}_b \mid \underline{R}_{ab})$ form a complete set so that the exact solution may be expanded in terms of these functions instead of the products $\mu_a^i(\underline{r}_a)\, \mu_b^j(\underline{r}_b)$

Thus the solution is expanded in the form

$$\Psi_{(\underline{r}_a, \underline{r}_b, \underline{R}_{ab})} = \sum_{\kappa \ell} F_{ij}^{\kappa \ell}(\underline{R}_{ab})\, \psi_{(\underline{r}_a, \underline{r}_b \mid \underline{R}_{ab})}^{ij} \qquad (1.3-13)$$

The derivation is carried through with the same approximations as for the method of distorted waves. If in the final result, the

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16.   C. Zener, Phys. Rev. 37, 556 (1931).

17.   R. S. Roy and M. E. Rose, Proc. Roy Soc. A149, 511 (1935)

18.   R. N. Schwartz, Z. I. Slawsky, and K. F. Hersfeld,
       J. Chem. Phys. 20, 1591 (1952).

19.   K. Takayanagi, Prog. Theoret. Phys. 8, 111 (1952).

20.   J. C. Beckerle, J. Chem. Phys. 21, 2034 (1953).

21.   R. N. Schwartz and K. F. Herzfeld, J. Chem. Phys. 22,
       767 (1954).

22.   J. C. Brout, J. Chem. Phys. 22, 1189 (1954).

$\Psi^{ij}(r_a, r_b \mid R_{ab})$ are replaced by their first order perturbation approximation in terms of the $\mu_a^i(r_a)$ and $\mu_b^j(r_b)$ there is obtained[23]

$$I_{ij}^{\kappa\ell}(g, \chi, \psi) = \frac{\mu^2}{h^4} \frac{K_{\kappa\ell}}{K_{ij}}$$

$$\times \left| \int\int \left[1 - \frac{2\mu}{h^2} \frac{\Phi_{ij,ij} - \Phi_{\kappa\ell,\kappa\ell}}{K_{ij}^2 - K_{\kappa\ell}^2} \right] \Phi_{ij,\kappa\ell} F_{ij}^{ij}(R_{ab}) f_{ij}^{\kappa\ell}(R_{ab}) \, d\tau \right|^2 \quad (1.3\text{-}14)$$

From this approximate expression, it may be seen that the result is similar to the distorted wave approximation, with full account taken of the distortion effect on the incoming and outgoing trajectories. Although the method appears well suited to the study of molecular collisions, it is difficult to apply since it requires a reasonably exact knowledge of the adiabatic functions. The excitation of He atoms by protons, and the electron capture from He by protons were studied some years ago by this method.[24] Interest in the method has recently been revived and semi-classical formulae for the total transition probability have been discussed in terms of the method by Bates et al.[25] It will become evident in Chapter II that our semi-classical description of the total collision process bears a close resemblance to this method.

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23. W. F. Mott and H. S. W. Massey, loc. cit. p. 156.

24. Massey and Smith, Proc. Roy. Soc. A 142, 142 (1933).

25. D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. A 216, 437 (1953).

1.4 History of the Semi-Classical Method for Studying Collision Problems.

Shortly after the introduction of quantum mechanical methods for studying inelastic collision phenomena, workers recognized the possibility of combining a classical description of the translational motion with a quantum description of the internal motions. In all of these studies the aim was to calculate the total probability of some change in the internal state, such as electronic excitation of ionization. The details of the trajectories in such studies were of secondary importance, in that the classical trajectory was used only to give the explicit time dependence of an interaction potential. This quantity is not sensitive to slight variations in the curvature of an orbit, so that in most cases straight line trajectories were found to be adequate for the problems considered. For application to the kinetic theory of gases, we require much more detailed and more accurate information about the shape of the trajectories. Since our theory is based on these earlier works, we shall review briefly some of the high points in the development of the semi-classical method.

Faxen and Holtzmark[26] were perhaps the first to emphasize the fact that the semi-classical method depended on a quantum mechanical separation of internal coordinates from the coordinates of relative motion. Any use of the semi-classical method must begin with a justification of this separation for the particular problem. Gaunt[27] made one of the first calculations of a collision problem by the semi-classical method when he considered the scattering of alpha particles. His results were quite poor, but it was later shown by Mott[28] that

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26. Faxen and Holtzmark, Zeit. f. Physik 45, 311 (1927).

27. Gaunt, Proc. Camb. Phil. Soc., 23, 732 (1927).

28. N. F. Mott, Proc. Camb. Phil. Soc. 27, 553 (1931).

the bad results were due to the approximation of some integrals rather than any inadequacy of the method. In the same paper, Mott put the semi-classical procedure on more firm ground by demonstrating its relation to the Born approximation of quantum mechanical scattering theory, and it was he who called it the method of impact parameters. Frame[29] calculated the probability of atomic excitation by fast alpha particles, using both the Born approximation and the semi-classical method. The agreement was good.

The first application of the method to inelastic molecular collisions was made by Zener[30] when he considered vibrational excitation produced by head on molecular collisions, and showed that the method was considerably more simple than the equivalent treatment by the method of distorted waves. Recently Widom and Bauer[31] have revived interest in the method by extending Zener's treatment to include collisions in which the impact parameter differs from zero. Bates[25] and coworkers have stressed the importance of the distortion of trajectories in slow collisions and have extended the method in this direction in connection with their work on the quantum mechanical method of perturbed stationary states.

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29.   J. W. Frame, Proc. Camb. Phil. Soc. 27, 511 (1931)

30.   C. Zener, Phys. Rev. 38, 277 (1931)

31.   B. Widom and S. H. Bauer, J. Chem. Phys. 21, 1670 (1953)

II. THE SEMI-CLASSICAL DESCRIPTION
OF A MOLECULAR COLLISION

In this chapter we present the semi-classical description of a general molecular collision. In section 2.1 we review the starting equations and present the basic assumptions of the method. Next we apply the equations to a description of collisions in which no internal transition takes place. In section 2.2 we extend the method to include a description of the internal wave functions and trajectories when a transition of internal coordinates takes place during the encounter.

2.1 Starting Equations and Elastic Encounters

Consider a system of two colliding molecules, "a" and "b", with masses m_a and m_b. The motion of the system may be described in terms of that of the center of mass of the complete system, the relative motion of the centers of mass of the two bodies and the motion of the individual molecules relative to their own centers of mass. Of these, the motion of the center of mass of the entire system is irrelevant and can always be separated out and the Schroedinger equation describing the two molecule system may be written in form[1].

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1. N. F. Mott and H. S. W. Massey, loc. cit. p. 139.

$$\left[H_a(\underline{r_a}) + H_b(\underline{r_b}) - \frac{\hbar^2}{2\mu} \nabla^2_{\underline{R}_{ab}} + \Phi(\underline{r_a}, \underline{r_b}, \underline{R}_{ab}) - E_{rel} \right] \Theta(\underline{r_a}, \underline{r_b}, \underline{R}_{ab}) = 0 \qquad (2.1\text{-}1)$$

Here $\underline{r}_a$ and $\underline{r}_b$ denote all of the coordinates necessary to specify the configurations of molecules a and b relative to their own mass centers, and H_a and H_b are the Hamiltonians of molecules a and b when they are isolated in space. $\underline{R}_{ab}$ gives the orientation of the center of mass of molecule b relative to that of molecule a, viewed in a coordinate system translating with the center of mass of the whole system, and E_{rel} is the total energy of the system relative to the center of mass. The quantity $\Phi(\underline{r_a}, \underline{r_b}, \underline{R}_{ab})$ is the potential energy of interaction of the molecules, and the reduced mass of the system μ is given by

$$\mu = \frac{m_a \, m_b}{m_a + m_b}$$

The internal Hamiltonians H_a and H_b may be used to define a set of eigenfunctions μ_a^i, μ_b^j and energies E_a^i, E_b^j describing the motions of the isolated molecules

$$H_a(\underline{r_a}) \left[\mu_a^i(\underline{r_a}) - E_a^i \right] = 0$$

$$H_b(\underline{r_b}) \left[\mu_b^j(\underline{r_b}) - E_b^j \right] = 0 \qquad (2.1\text{-}2)$$

The fact that only the <u>relative</u> separation of the two molecules appears in Eq. 2.2-1 indicates that the relative motion of the molecules may be viewed in terms of an equivalent one particle problem[2].

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2. MTGL. p. 49.

The information describing the motion of the two molecules in the center of mass coordinate system may be obtained by imagining that one molecule is fixed at the origin and that the other moves relative to it with the same intermolecular potential as before, providing only that the moving molecule is assumed to have a mass equal to the reduced mass of the two molecule system. The description of the internal motions of the two molecules is not altered by this changed point of view, since the relative coordinate system translates uniformly with the center of mass, but does not rotate with respect to axes fixed in space. Because of the conceptual simplicity of the one particle description of the encounter, we shall use it extensively in the rest of the discussion.

For the semi-classical solution of Eq. 2.1-1 we assume that a Born - Oppenheimer type separation[3,4] of the internal coordinates from the coordinates of relative motion may be used. That is, the solutions of Eq. 2.1-1 are assumed to be expressable as a product

$$\Theta^{(i)}(r_a, r_b, R_{ab}) = \psi_{int}^{(i j)}(r_a, r_b, R_{ab}) \chi^{(i)}(R_{ab})$$

where $\psi_{int}^{(i j)}(r_a, r_b, R_{ab})$ and $\chi^{(i)}(R_{ab})$ are given by the equations

$$\left[H_a(r_a) + H_b(r_b) - \Phi(r_a, r_b, R_{ab}) - E_{int}^{(i)}(R_{ab}) \right] \psi_{int}^{(i)}(r_a, r_b, R_{ab}) = 0 \qquad (2.1-3)$$

and

$$\frac{1}{\mu} \nabla_{R_{ab}}^2 \chi^{(i)}(R_{ab}) - \frac{2}{\hbar^2} \left[E_{int}^{(i)}(R_{ab}) - E_{rel} \right] \chi^{(i)}(R_{ab}) = 0 \qquad (2.1-4)$$

The wave function $\psi_{int}^{(i j)}(r_a, r_b, R_{ab})$ is not to be confused with the azimuthal angle of scattering ψ.

Equation 2.1-3 gives the wave functions and energies of the hypothetical situation in which the relative orientation   of the

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3.   M. Born and J. R. Oppenheimer, Ann. Phys. 84, 457 (1927)

4.   Derivations of the separation and ways of determining the error are further discussed in H. Pelzer and E. P. Wigner, Z. Physik. Chem. B 15 , 445 (1932) and MTGL p. 925.

molecules is held fixed. The wave functions $\psi_{int}^{ij}(\underline{r}_a, \underline{r}_b | \underline{R}_{ab})$ and energies $E_{int}^{ij}(\underline{R}_{ab})$ of this solution thus depend only parametrically on the intermolecular orientation $\underline{R}_{ab}$ The quantum numbers i and j represent all necessary quantum numbers for specifying the internal state. A representation is chosen such that ψ_{int}^{ij} becomes a simple product of the separate molecule wave functions as $\underline{R}_{ab}$ is increased to infinity. Thus

$$\lim_{\underline{R}_{ab} \to \infty} \psi_{int}^{ij}(\underline{r}_a, \underline{r}_b | \underline{R}_{ab}) = \mu_a^i(\underline{r}_a) \mu_b^j(\underline{r}_b) \qquad (2.1-5)$$

For this reason we refer to the ψ_{int}^{ij} as the "adiabatic clamped" solutions of the internal motions. The energies define a set of potential energy surfaces, one for each set of quantum numbers, which govern the relative motion of the moecules. Equation 2.1-4 then gives the quantum mechanical description of the relative motion of the molecules on such a potential energy surface. It is convenient to define two new quantities $\varphi^{ij}(\underline{R}_{ab})$ and E_{trans}^{ij} such that

$$\varphi^{ij}(\underline{R}_{ab}) = E_{int}^{ij}(\underline{R}_{ab}) - E_{int}^{ij}(\infty)$$

$$E_{trans}^{ij} = E_{rel} - E_{int}^{ij}(\infty) \qquad (2.1-6)$$

This is reasonable and useful since now $\varphi^{ij}(\underline{R}_{ab})$ vanishes as $|\underline{R}_{ab}|$ goes to infinity and is indeed the effective intermolecular potention, and E_{trans}^{ij} is the relative translational kinetic energy of the colliding system when the encounter begins.

$$E_{trans}^{ij} = \frac{1}{2} \mu g^2$$

With this notation Eq. 2.1-4 becomes

$$\frac{1}{\mu} \nabla_{\underline{R}_{ab}}^2 \chi_{trans}^{ij} - \frac{2}{\hbar^2} \left[\varphi^{ij}(\underline{R}_{ab}) - E_{trans}^{ij} \right] \chi_{trans}^{ij} = 0 \qquad (2.1-7)$$

The semi-classical formulation of the problem is completed by assuming that Eq. ?.1-7 for the relative motion of the molecules may be solved in the classical limit.

Now we are in a position to give the semi-classical description of the elastic collision between molecules which start out in the states u_a^i and u_b^j . The trajectory is given by the motion of a particle of mass μ moving in the potential field $\varphi^{ij}(\underline{R}_{ab})$ with initial conditions of energy and angular momentum given by the initial relative velocity g and collision parameter b . The wave functions describing the internal state of the molecules is given by the adiabatic clamped functions $\psi_{int}^{ij}(\underline{r}_a, \underline{r}_b | \underline{R}_{ab})$ evaluated along the trajectory.

2.2 Inelastic Encounters[5]

An inelastic encounter is described by assuming that a transition of the internal quantum state, say

$$\psi_{int}^{ij}(\underline{r}_a, \underline{r}_b | \underline{R}_{ab}) \longrightarrow \psi_{int}^{\kappa\ell}(\underline{r}_a, \underline{r}_b | \underline{R}_{ab})$$

takes place at some point along the trajectory. The subsequent relative motion is described by motion on the new potential energy surface $\varphi^{\kappa\ell}(\underline{R}_{ab})$ with boundary conditions determined by application of the classical conservation laws of energy and angular momentum at

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5.   Kallman and London, Z. Phys. Chem. **B2** , 207 (1929) give a
      thorough discussion of the many types of non adiabatic molecular
      collisions.

the point of transition. In part <u>a</u> of this section the probability of transition is discussed in terms of time dependent perturbation theory, and an approximate expression is presented for determining the relative probability that the transition took place at various points along the trajectory. In part <u>b</u> the use of the classical conservation laws for determining the new trajectory is discussed.

a)   The internal transition.

The classical elastic trajectories give the intermolecular separation R_{ab} as an explicit function of time, so that the method of time dependent perturbations[6] is indicated for an investigation of the probability of transition. One slight modification of the theory is necessary for our purposes, however. Ordinarily one takes for unperturbed wave functions the simple product functions corresponding to the non interacting system. Then one finds[6] that the probability that a system which at time $t = -\infty$ was in the pure initial state whose quantum numbers are specified by i and j is found in the final state specified by k and l at time t, is given by

$$P^{0}_{ij \to kl}(t) = \left| \frac{1}{i\hbar} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}[E_a^i + E_b^j - E_a^k - E_b^l]t'} (\mu_a^k \mu_b^l \mid \Phi_{ab} \mid \mu_a^i \mu_b^j) \, dt' \right|^2 \quad (2.2-1)$$

Here E_a^i, E_a^k, E_b^j, and E_b^l are the internal energies of the isolated molecules as defined in Eq. 2.1-2, and the matrix element in the intergrand is given by

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6.   P. A. M. Dirac, Proc. Roy. Soc. <u>A112</u>, 661 (1926) and <u>A114</u>, 243, (1927)
A derivation of the method is included in most elementary quantum mechanics texts, see for example, L. I. Schiff, <u>Quantum Mechanics</u>, McGraw Hill, 1949, p. 189.

$$(\mu_a^\kappa \mu_b^\ell \mid \Phi_{(\mathbf{r}_a, \mathbf{r}_b, R_{ab})} \mid \mu_a^i \mu_b^j) = \iint \mu_a^{\kappa*} \mu_b^{\ell*} \Phi_{(\mathbf{r}_a, \mathbf{r}_b, R_{ab})} \mu_a^i \mu_b^j \, d\mathbf{r}_a \, d\mathbf{r}_b$$

We suppose that $t = 0$ is taken at the distance of closest approach of the two molecules.

In our formulation of the collision problem in Sec. 2.1 we assumed that the encounters were nearly adiabatic, so that the adiabatic functions $\psi_{int}^{ij}(\mathbf{r}_a, \mathbf{r}_b, R_{ab})$ obtained by solution of Eq. 2.1-3 provide a more accurate description of the internal coordinates during the encounter than do the $u_a^i u_b^i$. Taking these adiabatic functions (which depend on time through R_{ab}) as a continuously changing set of unperturbed functions, it is shown in appendix I that the transition probability is given by

$$P_{ij \to \kappa\ell}^{(1)}(t) = \left| \int_{-\infty}^{t} \frac{e^{-\frac{i}{\hbar} \int_{0}^{t'} [E_{int}^{ij}[R_{ab}(s)] - E_{int}^{\kappa\ell}[R_{ab}(s)]] \, ds}}{E_{int}^{ij}[R_{ab}(t')] - E_{int}^{\kappa\ell}[R_{ab}(t')]} (\psi_{int}^{\kappa\ell} \mid \frac{d\Phi}{dt} \mid \psi^{ij}) \, dt' \right|^2 \qquad (2.2-2)$$

Here the superscript (1) on the transition probability indicates that the adiabatic wave functions and energies are taken for the unperturbed set. Note that now the time derivative of the interaction potential appears explicitly, and that the energies of the unperturbed states vary with the time through R_{ab}.

The most interesting feature of this form of the transition probability is the appearance of the time rate of change of the potential, rather than the potential itself, as in the expression for $P_{ij \to \kappa\ell}^{(0)}(t)$. In the limit of an infinitely slow encounter we expect no transitions at all, for although the wave functions are distorted by the interaction potential during such an encounter, they return adiabatically to their initial state as the interaction decreases.

That this is indeed the case may be seen by writing Eq. 2. 2-2 as a function of the arc length along the trajectory. s, instead of as a function of the time. Then

$$P_{ij \to k\ell}^{(1)}(s) = \left| \int_{-\infty}^{s} \frac{e^{-\frac{i}{\hbar}\int_{0}^{t(s)} \Delta E_{ij}^{k\ell}(s) dt}}{\Delta E_{ij}^{k\ell}(s')} \left(\psi_{int}^{k\ell} \left| \frac{d\Phi}{ds'} \right| \psi_{int}^{ij} \right) ds' \right|^{2}$$

(2. 2-2b)

Now, as the relative velocity vanishes, a small change in s corresponds to a large change in the time t(s) so that the exponential term oscillates more and more rapidly as the relative velocity is decreased. Thus successive contributions of the integrand tend to cancel, and it may be seen at least qualitatively that as the relative velocity vanishes, the integral goes to zero.

Thus the adiabatic distortion of the wave functions has been separated out, and we are looking only for transitions among such distorted wave functions, which are caused by the relative velocity. This may be visualized as transitions among the distorted potential energy surfaces of the system, as in Fig. 2.2-1.
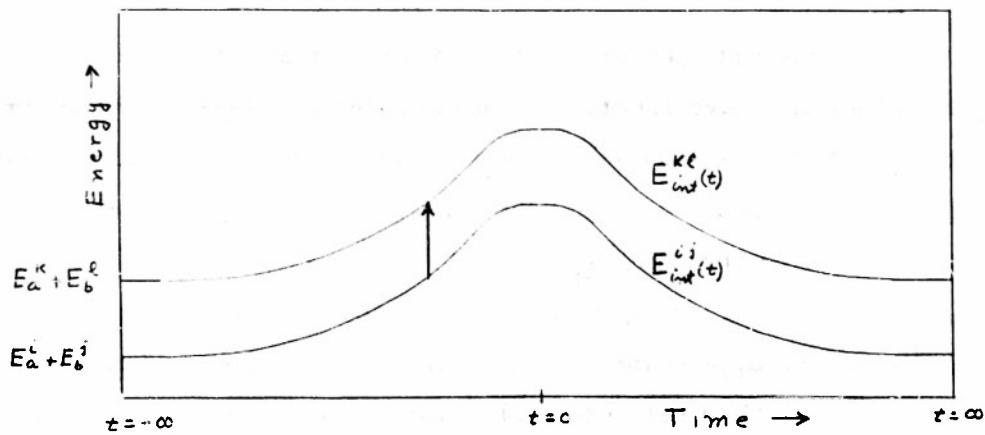
Fig. 2. 2-1 A quantum transition of internal coordinates viewed as a jump between potential energy surfaces.

Here we picture schematically several potential energy surfaces of the system during an encounter as a function of time. The function $P^{(l)}_{ij \to kl}(t)$ gives the probability that a system which started out on the ij energy surface will at time t have jumped across to the kl energy surface. Bohm[7] points out that this formulation of the time dependent perturbation in terms of adiabatic functions allows one to consider systems in which the perturbation potential is large, as long as the rate of change of the potential is small.

In most collision problems, one asks about the total probability that a transition has taken place due to a perturbation during the whole course of the collision; that is, one is interested in the value of $P^{(l)}_{ij \to kl}(\infty)$. We, however, shall be interested in the additional question as to the relative probability that the transition took place in given short time intervals during the time the perturbation was acting. From Eq. 2.2-2 we might say that the probability that the transition took place between time t and $t + \delta t$ is just

$$\frac{d\, P^{(l)}_{ij \to kl}(t)}{dt}\, \delta t$$

but in quantum mechanics we are limited in the kind of questions we may ask by the uncertainty principle. In one form[8] this says that the product of the uncertainty in a measurement of the energy of a system, δE, and the uncertainty in the time at which the measurement was made, δt, are related by the expression

$$\delta E \cdot \delta t \geq \hbar$$

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7.   D. Bohm, Quantum Theory, Prentice-Hall, 1951, p. 496.

8.   L. I. Schiff, loc. cit. p. 7.

In our transition probability we are asking about two states of the system differing in energy by an amount

$$\delta E = E_{int}^{\kappa\ell} - E_{int}^{ij}$$

hence we cannot expect the expression

$$\frac{d\,P_{ij\to\kappa\ell}^{(i)}(t)}{dt}\,\delta t$$

to give meaningful results for times δt less than about

$$\left| \frac{\hbar}{E_{int}^{\kappa\ell} - E_{int}^{ij}} \right|$$

In Sec. 3.2 where we calculate sample curves of $P_{ij\to\kappa\ell}^{0}(t)$ and $P_{ij\to\kappa\ell}^{(l)}(t)$ for the special case of rigid, linear molecules with ideal electric dipoles, we find that this is indeed the case, and that these curves oscillate with a period equal to $\frac{\hbar}{\delta E}$ while going from zero at $t=-\infty$ to the final value $P_{ij\to\kappa\ell}^{(l)}(\infty)$ at $t=\infty$. Such oscillations make $\frac{d\,P_{ij\to\kappa\ell}^{(l)}(t)}{dt}$ negative at some points during the encounter, which interpreted naively would indicate a negative probability of transition in those regions.

Since we are allowed, quantum mechanically speaking, to ask about the probability that a transition has taken place in a time interval corresponding to one such complete oscillation, one might expect to construct a classical analogue of the transition probability by drawing a smooth curve through points on the oscillating curve separated by times

$$\delta t = \left| \frac{\hbar}{E_{int}^{\kappa\ell} - E_{int}^{ij}} \right|$$

This was attempted, but for the sample curves calculated, the

procedure was not satisfactory in that the resulting curve for the integrated transition probability still oscillated and passed through a maximum in the vicinity of the distance of closest approach. (It is difficult to interpret a decrease in the integrated probability after it has passed through a maximum) In any case we were unable to obtain satisfactory criteria for constructing a classically satisfactory approximation to the curve $P''_{(t)_{c, \to \kappa \ell}}$ by considerations of this sort.

As a next approach, one might try to obtain a series expansion of the transition probability or of its derivative. The transition probability is approximately of the form

$$P_{(y)} = \left| \int_{-\infty}^{y} e^{-i\eta} f_{(\eta)} \, d\eta \right|^{2} \tag{2.2-3}$$

Differentiating with respect to y , this may be written

$$\frac{d P_{(y)}}{d y} = f_{(y)} \, 2 \, Re \left[e^{-iy} \int_{\infty}^{y} e^{i\eta} f_{(\eta)} \, d\eta \right] \tag{2.2-4}$$

Integrating by parts repeatedly and noting that all derivatives of the function $f(y)$ vanish as $y \to \infty$ we obtain

$$\frac{d P_{(y)}}{d y} = 2 \, f_{(y)} \left[f'_{(y)} - f'''_{(y)} + f^{\underline{\pi}}_{(y)} - \cdots \right] \tag{2.2-5}$$

since $f(y)$ for a dipole-dipole interaction is of the form

$$\frac{y}{[c^{2}+y^{2}]^{5/2}}$$

each of the products of this series is an odd function of y so that approximating $P_{(y)}$ by any finite number of terms in the series gives the unsatisfactory result that

$$P_{(\infty)} = \int_{-\infty}^{\infty} \frac{d P_{ij}}{d \jmath} \, d\jmath = 0$$

In the absence of a satisfactory derivation of the classical analogue of $P_{ij \to \kappa\ell}^{(1)}(t)$ .we suggest that the following function may serve as a satisfactory approximation[9]

$$P_{ij \to \kappa\ell}^{class}(t) = \frac{\int_{-\infty}^{t} \left(\psi_{int}^{\kappa\ell} \left| \frac{d\Phi}{dt} \right| \psi_{int}^{ij} \right)^{2} \left| \frac{dR}{dt} \right|^{-1} dt}{\int_{-\infty}^{\infty} \left(\psi_{int}^{\kappa\ell} \left| \frac{d\Phi}{dt} \right| \psi_{int}^{ij} \right)^{2} \left| \frac{dR}{dt} \right|^{2} dt} \; P_{ij \to \kappa\ell}^{(1)} \tag{2.2-6}$$

This function has the following desirable properties:

1. It is zero at $t = -\infty$ and equal to $P_{ij \to \kappa\ell}^{(1)}$ at $t = +\infty$ in agreement with the quantum mechanical formula.

2. It is monotonic increasing over the entire range, corresponding to the classical picture that if transitions are rare, there is negligible chance of multiple or reverse transitions, so that there ought to be a steadily increasing probability of finding the system in the final state.

3. If the time rate of change of the interaction potential is either symmetric or antisymmetric about $t = 0$, Eq. 2.2-6 gives

$$P_{ij \to \kappa\ell}^{class}{}_{(t=0)} = \frac{1}{2} \, P_{ij \to \kappa\ell}^{class}{}_{(t=\infty)}$$

Since elastic trajectories are symmetric in shape about the distance of closest approach,

$$\frac{d \Phi_{(t)}}{dt} = - \frac{d \Phi_{(-t)}}{dt} \tag{2.2-7}$$

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9. The classical analogue of the transition probability might profitably be investigated from the point of view of Wigner's distribution function formulation of quantum statistical mechanics, but no work has been done in this direction. This method is described in E.P. Wigner, Phys. Rev. 40, 479 (1932) and in J. H. Irving and R. W. Zwanzig, J. Chem. Phys. 19, 1173, (1951).

and Eq. 2.2-6 says that there is equal probability of the transition occurring on the approaching and the receding parts of a trajectory. This is justified as a first approximation by noting that due to the absolute square operation, $P_{c_j \to k\ell}^{(l)}(t)$ is unchanged if $\frac{d\Phi}{dt}$ is replaced by $-\frac{d\Phi}{dt}$. That is, to a first approximation, the quantum mechanics does not care about the actual sign of this quantity, and we are led to expect equivalent behavior on the two halves of a symmetric trajectory[10].

4. The transition probability increases most rapidly in regions where the perturbation potential is changing most rapidly in time. This is consistent with the adiabatic theorem, and the quadratic dependence on $\frac{d\Phi}{dt}$ is suggested by the absolute square operation in $P_{c_j \to k}^{(l)}(t)$.

5. The factor $\left|\frac{dR}{dt}\right|^{-1}$ in the integrand makes $P_{c_j \to k\ell}^{class}(t)$ agree with the general form of $P_{c_j \to k\ell}^{(l)}(t)$ when they are considered as functions of the intermolecular distance R rather than the time[11]. That is, if $P_{c_j \to k\ell}^{(l)}(t)$ is expressed as an integral over R, it takes the form

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10. The other function one might guess,
$$P_{c_j \to k\ell}^{class}(t) = \frac{\left|\int_a^t (\psi_{c\omega}^{k\ell} | \frac{d\Phi}{dt} | \psi_{c\omega}^{c_j}) \, dt\right|^2}{\left|\int_{-\infty}^{\infty} (\psi_{c\omega}^{k\ell} | \frac{d\Phi}{dt} | \psi_{c\omega}^{c_j}) \, dt\right|^2} F_{c_j \to k\ell}^{(l)}(\infty)$$
is unsatisfactory from this point of view, since it gives $P_{c_j \to k\ell}^{class}(0) = \frac{1}{4} P_{c_j \to k\ell}^{class}(\infty)$.

11. Omission of the factor $\left|\frac{dR}{dt}\right|^{-1}$ in the definition of $P_{c_j \to k\ell}^{class}(t)$ in Eq. 2.2-7, thus giving qualitative agreement with the form of $P_{c_j \to k\ell}^{(l)}$ expressed as an integral over the time would have resulted in an anomaly when $P_{c_j \to k\ell}^{class}(t)$ was considered as an integral over R. That is, we would have obtained
$$P_{c_j \to k\ell}^{class}(R) = \frac{\int_{-\infty}^{R} (\psi_{c\omega}^{k\ell} | \frac{d\Phi}{dR} | \psi_{c\omega}^{c_j})^2 | \frac{dR}{dt} | \, dR}{\int_{-\infty}^{\infty} (\psi_{c\omega}^{k\ell} | \frac{d\Phi}{dR} | \psi_{c\omega}^{c_j})^2 | \frac{dR}{dt} | \, dR} P_{c_j \to k\ell}^{(l)}(\infty)$$
Since at the distance of closest approach $\frac{dR}{dt} = 0$ this would imply a vanishing probability that the transition took place between R and $R+ dR$ about the distance of closest approach. The quantum mechanical formula, Eq. 2.2-8, indicates that this is actually a very likely region for the transition.

$$P_{ij \to \kappa\ell}^{(i)}(R) = \left| \int_{-\infty}^{R} \frac{e^{-\frac{i}{\hbar}\int_{-\infty}^{t(R)} \Delta E_{ij}^{\kappa\ell}(\theta) d\theta}}{\Delta E_{ij}^{\kappa\ell}(R)} \left(\psi_{int}^{\kappa\ell} \left| \frac{d\Phi}{dR} \right| \psi_{int}^{ij} \right) dR \right|^2 \qquad (2.2\text{-}8)$$

and $P_{ij \to \kappa\ell}^{class}(t)$ the form

$$P_{ij \to \kappa\ell}^{class}(R) = \frac{\int_{-\infty}^{R} \left(\psi_{int}^{\kappa\ell} \left| \frac{d\Phi}{dR} \right| \psi_{int}^{ij} \right)^2 dR}{\int_{-\infty}^{\infty} \left(\psi_{int}^{\kappa\ell} \left| \frac{d\Phi}{dR} \right| \psi_{int}^{ij} \right)^2 dR} \; P_{ij \to \kappa\ell}^{(i)}(\infty) \qquad (2.2\text{-}9)$$

Here the upper limit of the integrations indicates an integration along the trajectory; since in general R passes through a minimum, then increases to ∞, the integral will have two branches when the upper limit corresponds to a point on the trajectory beyond the distance of closest approach.

In section 3.3 sample calculations of $P_{ij \to \kappa\ell}^{class}(t)$ and $\frac{d}{dt}\left[P_{ij \to \kappa\ell}^{class} \right]$ are plotted for the special case of rigid, linear polar molecules, and are compared with the functions $P_{ij \to \kappa\ell}^{(0)}(t)$ and $P_{ij \to \kappa\ell}^{(i)}(t)$.

This completes the semi-classical description of the internal transition on an inelastic trajectory. The expression

$$\frac{d}{dt}\left[P_{ij \to \kappa\ell}^{class}(t) \right] dt$$

gives the probability that the transition takes place between time t and $t + dt$ during the encounter, and

$$\int_{-\infty}^{\infty} \frac{d}{dt}\left[P_{ij \to \kappa\ell}^{class}(t) \right] dt = P_{ij \to \kappa\ell}^{class}(\infty) = P_{ij \to \kappa\ell}^{t}$$

gives the total probability that the transition takes place during the encounter.

b) The inelastic trajectory.

If we suppose that at some point along the trajectory the internal wave function changes from $\psi_{int}^{ij}(\underline{r_a}, \underline{r_b}, \underline{R_{ab}})$ to $\psi_{int}^{\kappa\ell}(\underline{r_a}, \underline{r_b}, \underline{R_{ab}})$, then the relative motion of the molecules in this region reflects the sudden shift from the potential energy surface $\phi^{ij}(\underline{R_{ab}})$ to the

new surface $\varphi^{\kappa\ell}(R_{ab})$. The boundary conditions of energy and angular momentum necessary for a precise description of the motion in the new potential field $\varphi^{\kappa\ell}(R_{ab})$ are deduced from the classical conservation laws of energy and angular momentum.

Let us denote the equivalent one particle trajectory before the transition by T^{ij} and that after the transition by T^{kl}. The quantities necessary for specifying the initial conditions of T^{kl} may be defined with reference to Fig. 2.2-2 where we picture the details of the trajectory at the moment of inelastic transfer.
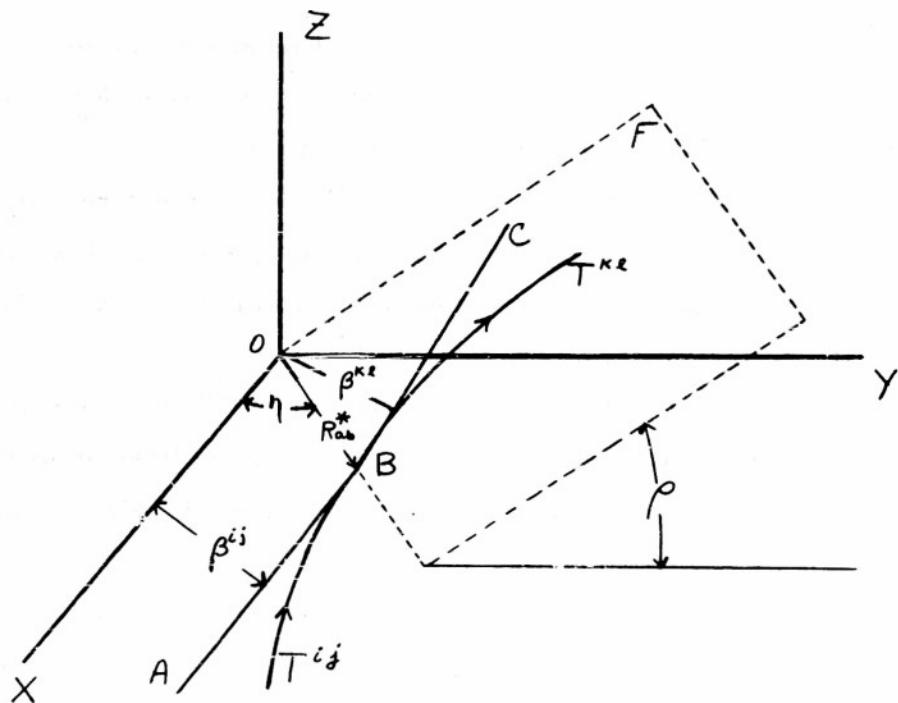
Fig. 2.2-2 Details of a trajectory at the moment of inelastic transfer.

Since we are required simply to determine the orientation of T^{kl} relative to T^{ij}, the coordinate system we use at this point is quite arbitrary, as long as it is defined in terms of the trajectory before the transition, T^{ij}.

Suppose the transition takes place at point B where $|R_{ab}| = R_{ab}^*$ Let AB and BC be tangents to T^{ij} and T^{kl} at R_{ab}, and let AB lie in the xy plane, parallel to the x axis. Let the perpendicular distances of AB and BC from the origin be $\beta^i(R_{ab}^*)$ and $\beta^*(R_{ab}^*)$ Note that β is an instantaneous analogue of the collision parameter b, in that for large values of R_{ab}, $\beta = b$. Let the origin and line BC determine the plane F which intersects the xy plane along OB $= R_{ab}^*$, and makes an angle ρ with the xy plane. Finally, let η be the angle which R_{ab}^* makes with the x axis. In case the effective potentials $\varphi(R_{ab})$ are spherically symmetric, the trajectory T^{ij} will lie entirely in the xy plane and T^{kl} will lie entirely in the F plane. In this case it would be convenient to fix the coordinate system by making the x axis parallel to the initial asymptote of T^{ij}.

The initial conditions of the new trajectory T^{kl} may now be specified by three quantities: ρ giving the inclination of the F plane, $\beta^{kl}(R_{ab}^*)$ locating the trajectory in the F plane, and $\upsilon^{kl}(R_{ab}^*)$ giving the new relative velocity. These three quantities may be determined by application of the classical conservation laws of energy and angular momentum applied at the point of transition.

1. <u>The relative velocity after the transition:</u> $\quad \mathcal{V}^{\kappa\ell}_{(R^*_{ab})}$

In terms of quantities already defined, the conservation of energy relative to the center of mass of the whole system may be written

$$E_{rel} = E_a^i + E_b^j + \varphi^{ij}_{(R_{ab})} + \frac{1}{2}\mu\left[\mathcal{V}^{ij}_{(R_{ab})}\right]^2$$

$$= E_a^j + E_b^\kappa + \varphi^{\kappa\ell}_{(R_{ab})} + \frac{1}{2}\mu\left[\mathcal{V}^{\kappa\ell}_{(R_{ab})}\right]^2 \tag{2.2-10}$$

From Eq. 2.1-6

$$E_a^i + E_b^j + \varphi^{ij}_{(R_{ab})} = E_{rel}^{ij}(R_{ab})$$

so the first three terms in the energy expression represent the total internal energy of the adiabatic clamped system. The last term containing the relative velocity $v^{ij}(R^*_{ab})$, gives the kinetic energy relative to the moving center of mass of the two molecule system. Eq. 2.2-10 may be solved immediately for the relative velocity after the transition:

$$\mathcal{V}^{\kappa\ell}_{(R^*_{ab})} = \left\{\frac{2}{\mu}\left[E_a^i - E_a^\kappa + E_b^j - E_b^\ell + \varphi^{ij}_{(R^*_{ab})} - \varphi^{\kappa\ell}_{(R^*_{ab})} + \frac{1}{2}\mu\,\mathcal{V}^{ij}_{(R^*_{ab})}^2\right]\right\}^{1/2} \tag{2.2-11}$$

In case this velocity is imaginary, we conclude that the transition is energetically forbidden, so this result constitutes a sort of "selection" on the transition.

2. <u>Orientation of the trajectory in plane F:</u> $\quad \beta^{\kappa\ell}_{(R^*_{ab})}$

The conservation of angular momentum may be expressed as

$$\underline{L} = \underline{\ell}_a^i{}_{(R_{ab})} + \underline{\ell}_b^j{}_{(R_{ab})} + \underline{\ell}_{ang}^{ij}{}_{(R_{ab})} = \underline{\ell}_a^\kappa + \underline{\ell}_b^\ell + \underline{\ell}_{ang}^{\kappa\ell}{}_{(R_{ab})} \tag{2.2-12}$$

Here $\underline{l}_a^i$ $\underline{l}_b^j$, $\underline{l}_a^K$ and $\underline{l}_b^l$ are the internal angular momenta associated with molecules a and b before and after the transition, and $\underline{l}_{trans}^{ij}(R_{ab})$ and $\underline{l}_{trans}^{Kl}(R_{ab})$ are the angular momenta associated with the relative translational motion of the molecules. For example

$$\underline{l}_{trans}^{ij}(R_{ab}) = \mu \left[\underline{R}_{ab} \times \underline{v}^{ij}(R_{ab}) \right] \tag{2.2-13}$$

Equation 2.2-12 may be used to determine $\beta^{Kl}(R_{ab}^*)$ as follows: By definition,

$$\left| \underline{l}_{trans}^{Kl}(R_{ab}^*) \right| = \left| \mu \left[\underline{R}_{ab}^* \times v^{Kl}(R_{ab}^*) \right] \right| = \mu \beta^{Kl}(R_{ab}^*) \, v^{Kl}(R_{ab}^*) \tag{2.2-14}$$

So if we assume for the moment that we are able to solve Eq. 2.2-12 for $\underline{l}_{trans}^{Kl}(R_{ab}^*)$, then we have, simply,

$$\beta^{Kl}(R_{ab}^*) = \frac{\left| \underline{l}_{trans}^{Kl}(R_{ab}^*) \right|}{\mu \, v^{Kl}(R_{ab}^*)} \tag{2.2-15}$$

The significance of this result as far as determining the orientation of BC in plane F may be seen by reference to Fig. 2.2-3 where we picture the situation in plane F.
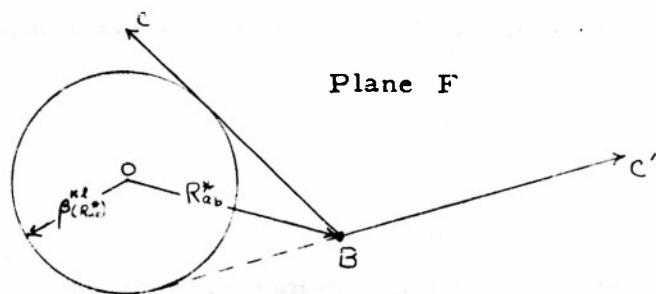

Fig. 2.2-3 The trajectory in the new plane immediately after the transition.

From the definition of $\beta^{\kappa\ell}(\underline{R}_{ab}^*)$, BC is to be constructed so as to be tangent to the circle of radius $\beta^{\kappa\ell}(\underline{R}_{ab}^*)$ centered at the origin and lying in plane F. From Fig. 2.2-3 it is apparent that if the point B lies outside the circle there are two such possible tangents, both of which give the correct translational angular momentum. In case $\beta^{\kappa\ell}(\underline{R}_{ab}^*)$ is greater than R^*_{ab}, so that point B lies inside the circle, no satisfactory trajectory can be constructed at point B which will be consistent with the conservation of angular momentum. This constitutes a second selection rule on the transition at point B.

When the transition is allowed, the choice between the two possible paths is really unique. This may be argued as follows: Let us suppose that the change in angular momentum in the transition specified by ij → kl approaches zero.

In the limit of no transition a diagram like Fig. 2.2-2 may still be constructed with the two possible trajectories, but now the equations of motion clearly require that the particle continue on the smooth trajectory rather than taking the abrupt change in direction which would also be consistent with the angular momentum of the system. That is, an approaching particle cannot suddenly jump to a receding trajectory. The finite transition may be viewed as a series of infinitesimal transitions resulting in a gradual distortion of the trajectory, during which the distinction between approaching and receding paths remains clear at every step. For the finite transition this simply implies that if T^{ij} at $\underline{R}_{ab}^*$ is an approaching path, then T^{kl} is to be chosen as the approaching path, and similarly for receding paths.

3. Orientation of the plane F: ρ

By the definition of the angular momentum, the plane F in which the new trajectory lies must now be so oriented as to be perpendicular to the angular momentum vector $\ell_{trans}^{\kappa\ell}(R_{ab}^{*})$ of the new trajectory. A difficulty arises, however, due to the fact that it is not possible to construct a trajectory through B which has an arbitrary angular momentum with respect to the point 0. That is, the expression

$$\ell_{trans}^{\kappa\ell}(R_{ab}^{*}) = \mu \left[R_{ab}^{*} \times \underline{v}^{\kappa\ell}(R_{ab}^{*}) \right]$$

cannot be solved for $\underline{v}^{\kappa\ell}(R_{ab}^{*})$ except in the rather special case that $\ell_{trans}^{\kappa\ell}(R_{ab}^{*})$ is perpendicular to R_{ab}^{*}. This constitutes a strong selection rule on classical transitions in which the internal angular momentum goes from ℓ_a^{i} and ℓ_b^{j} to ℓ_a^{κ} and ℓ_b^{ℓ}. Unless the net change of the component of the internal angular momenta along the radius vector R_{ab}^{*} is zero, the transition is forbidden.

When the transition is defined quantum mechanically, however, the angular momenta of the initial and final states are not completely specified, so that in the correspondence limit a single quantum mechanical transition corresponds to a whole family of classical transitions, and the significance of this selection rule is somewhat modified. This may be seen by considering the two general cases which arise when we solve Eq. 2.2-12 for $\ell_{trans}^{\kappa\ell}(R_{ab}^{*})$.

The simplest solution of this equation arises when we consider a transition in which the angular momentum associated with the internal motions remains unchanged, as is the case for example in a pure vibrational transition. In this case Eq. 2.2-12 immediately gives the result that $\ell_{trans}^{\kappa\ell}(R_{ab}^{*})$ is colinear with $\ell_{trans}^{ij}(R_{ab}^{*})$ so that the plane F coincides with the xy plane and the angle ρ is zero. Such a transition is always allowed.

When the internal transition does involve a change in the internal angular momenta, as in electronic or rotational transitions, it is necessary to consider the internal angular momentum of the quantum mechanical systems in the light of the correspondence principle[12]. Since the quantum mechanical operators for the x, y, and z components of the angular momentum do not commute[13], it is not possible in quantum mechanics to specify the angular momentum of a system precisely. It is possible, however, to specify the square of the total angular momentum and an arbitrary component, say in the z direction.

The situation is illustrated in Fig. 2.2-4.
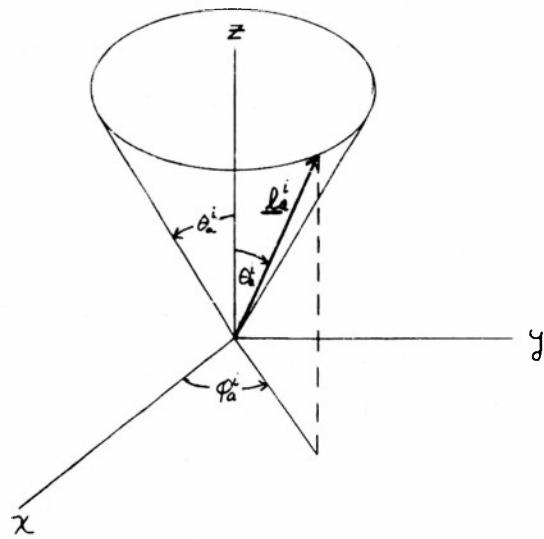
Fig. 2.2-4 Classical and quantum mechanical descriptions of the angular momentum.

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12. L. I. Schiff, loc. cit., p. 16.

13. H. Eyring, J. Walter and G. Kimball, Quantum Chemistry, Wiley, 1944, p. 39.

Classically the vector ℓ_a^i is precisely specified by $|\underline{\ell}_a^i|$, the polar angle θ_a^i and the azimuthal angle φ_a^i. Quantum mechanically we may specify only the length $|\underline{\ell}_a^i|$ and one component, say the z component given by the angle θ_a^i. In the correspondence limit the azimuthal angle φ_a^i is completely uncertain, so there is equal probability that the angular momentum vector lies anywhere in the cone of half angle θ_a^i. Thus the single quantum mechanical state corresponds to a whole family of classical states, and a quantum mechanical transition of the angular momentum vector between two such cones corresponds to a doubly infinite set of classical transitions. It is the composite behavior of this family of classical transitions which corresponds to behavior of the single quantum mechanical transition.

Thus if the quantum mechanical transition in which $\psi_{int}^{ij} \rightarrow \psi_{int}^{kl}$ involves a change in angular momentum, Eq. 2.2-12 may not be solved uniquely for $\underline{\ell}_{trans}^{kl}(\underline{R}_{ab}^*)$. Instead there is obtained a family of solutions corresponding to an equal probability distribution of the classical variables $\varphi_a^i, \varphi_b^j, \varphi_a^k$ and φ_b^l. All members of this family which are perpendicular to R^*_{ab}, hence which are consistent with the conservation of angular momentum, are used to construct final trajectories T^{kl}. Originating from every point of T^{ij}, then, we expect a family of final trajectories T^{kl}.

Illustration of this principle in the general case is difficult, because the coordinate system in which we analyze the transition (Fig. 2.2-1) is not in general fixed in space so that analysis of the angular momentum vectors in it would be very complicated. Consider the special case which arises when $\varphi^{ij}(\underline{R}_{ab})$ is spherically symmetric. Then the entire trajectory T^{ij} lies in the xy plane and the coordinate system is fixed in space so that the z direction may be taken as the axis along which components of all internal angular momenta are known precisely. In Chapter III it is shown that

the relative motion of rigid, linear polar molecules may be approximated by such a spherical potential, so the case is of considerable physical interest.

The restriction that $\ell_{tran}^{\kappa\rho}(R_{ab})$ be perpendicular to $\underline{R}^*_{ab}$ may be expressed in the form

$$\frac{(\ell_a^\kappa + \ell_b^\ell)_x - (\ell_a^i + \ell_b^j)_x}{(\ell_a^\kappa + \ell_b^\ell)_y - (\ell_a^i + \ell_b^j)_y} = -\tan\eta \qquad (2.2-16)$$

where, for example

$$(\ell_a^i)_x = |\ell_a^i| \cos\theta_a^i \cos\varphi_a^i$$

This result may be derived immediately from the conservation of the component of the angular momentum along OB, noting that the trajectory angular momenta have zero component along this direction. Equation 2.2-16 implies a relation among the four azimuthal angles φ_a^i, φ_b^j, φ_a^κ and φ_b^ℓ, so may be looked upon as a third selection rule which modifies application of the correspondence principle.

That this selection rule limits the family of T^{kl} diverging from point b, but never entirely forbids the transition may be seen by rewriting Eq. 2.2-12 in the form

$$|\ell_a^\kappa| \sin\theta_a^\kappa \left[\cos\varphi_a^\kappa + \tan\eta \sin\varphi_a^\kappa\right]$$

$$+ |\ell_b^\ell| \sin\theta_b^\ell \left[\cos\varphi_b^\ell + \tan\eta \sin\varphi_b^\ell\right]$$

$$- |\ell_a^i| \sin\theta_a^i \left[\cos\varphi_a^i + \tan\eta \sin\varphi_a^i\right] \qquad (2.2-17)$$

$$- |\ell_b^j| \sin\theta_b^j \left[\cos\varphi_b^j + \tan\eta \sin\varphi_b^j\right] = 0$$

Clearly

$$\cot\varphi_a^i = \cot\varphi_b^j = \cot\varphi_a^\kappa = \cot\varphi_b^\ell = -\tan\eta$$

is always an acceptable solution of this equation, for arbitrary η.

Thus for any internal transition, one or more solutions of the angular momentum equation (Eq. 2.2-12) may be obtained which give values of $\ell_{trans}^{\kappa\ell}(\underline{R}_{ab}^{x})$ satisfactory for determining $\beta^{\kappa\ell}(\underline{R}_{ab}^{*})$ and the angle ρ. If there is only one resulting trajectory, its probability is given by the change in the transition probability $P_{i\rightarrow\kappa\ell}^{class}(t)$ over that increment of the initial trajectory T^{ij} at which the transition occurred, as discussed in Sec. 2.1. If there is a family of resulting trajectories, the probability of the entire family is determined by this change of the transition probability, and the distribution of probability within the family is obtained by assuming that all values of the azimuthal angles φ_{a}^{i}, φ_{b}^{j}, φ_{a}^{κ} and φ_{b}^{ℓ} which are consistent with Eq. 2.2-12 are equally probable.

Thus we have a complete and unique method for constructing all possible trajectories in molecular collisions and of assigning a relative probability to each of them.

In the general case of transitions involving a change in the internal angular momentum there will always be some relation of the sort given in Eq. 2.2-16 relating the geometric location of the transition on the trajectory and the four azimuthal angles φ_{a}^{i}, φ_{b}^{j}, φ_{a}^{κ} and φ_{b}^{ℓ}. Thus if we ask about a particular quantum mechanical transition at some specified small interval along the trajectory, any three of these azimuthal angles may be considered as independent variables, say φ_{a}^{i}, φ_{b}^{j} and φ_{a}^{κ}. For each choice of these three angles, we may solve Eq. 2.2-15 for a value of $\beta^{\kappa\ell}(\underline{R}_{ab}^{*}, \varphi_{a}^{i}, \varphi_{b}^{j}, \varphi_{a}^{\kappa})$ and determine the angle $\rho(\underline{R}_{ab}^{*}, \varphi_{a}^{i}, \varphi_{b}^{j}, \varphi_{a}^{\kappa})$ by requiring that the plane F be perpendicular to the new trajectory

angular momentum. The family of final trajectories resulting from a transition which takes place between time t and $t + dt$ along the trajectory may be thought of as a function of the three azimuthal angles and the time, so we may write

$$T^{\kappa\ell} = T^{\kappa\ell}(\varphi_a^i, \varphi_b^j, \varphi_a^\kappa, t) .$$

According to the correspondence principle there is equal probability that these angles have any value between 0 and 2π, so if we wish to consider any function of the trajectory, $F(T^{\kappa\ell})$, its value averaged over the family of trajectories resulting from the quantum transition at time t may be written

$$\overline{F[T^{\kappa\ell}_{(t)}]} = \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} F[T^{\kappa\ell}(\varphi_a^i, \varphi_b^j, \varphi_a^\kappa, t)]\, d\varphi_a^i\, d\varphi_b^j\, d\varphi_a^\kappa \tag{2.2-18}$$

For example, the average value of $\rho_{(t)}$ is given by

$$\overline{\rho_{(t)}} = \frac{1}{8\pi^3} \int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \rho(\varphi_a^i, \varphi_b^j, \varphi_a^\kappa, t)\, d\varphi_a^i\, d\varphi_b^j\, d\varphi_a^\kappa \tag{2.2-19}$$

The probability that the transition occurred in the time interval dt is given by $\dfrac{d P_{ij \to \kappa\ell}^{class}(t)}{dt}$ so the average value of the quantity $F(T^{\kappa\ell})$ for all possible final trajectories resulting from a single encounter is given by

$$\overline{F}_{ij \to \kappa\ell} = \frac{1}{8\pi^3} \frac{1}{P_{ij\kappa\ell}^{(t)}(\infty)} \int_{-\infty}^{\infty}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} \frac{d P_{ij \to \kappa\ell}^{class}(t)}{dt} F[T^{\kappa\ell}(\varphi_a^i, \varphi_b^j, \varphi_a^\kappa, t)]\, d\varphi_a^i\, d\varphi_b^j\, d\varphi_a^\kappa\, dt \tag{2.2-20}$$

From the selection rules resulting from the conservation of energy and the magnitude of the angular momentum, it is to be remembered that those final trajectories T^{kl} are forbidden which give imaginary velocities $\nu^{\kappa\ell}$ or values of $\beta^{\kappa\ell}$ which are less than the intermolecular separation R.

III. SAMPLE CALCULATIONS FOR RIGID LINEAR
POLAR MOLECULES

In this chapter we illustrate the general theory derived in
Chapter II by making sample calculations relevant to the study of
rotational energy transfer in collisions between rigid linear mole-
cules containing ideal electric dipoles. In order to be specific,
actual numerical results will be given, using molecular constants
for HCl molecules.

An approximate spherically symmetric potential energy function
for describing the relative motion of the molecules is presented in
terms of London's solution of the adiabatic clamped equations. The
form of these potentials suggests why the viscosity of polar gases
actually can be described by the present theory for spherical
molecules.

The various transition probabilities $P_{ij \to \kappa \ell}^{(i)}(t)$, $P_{ij \to \kappa \ell}^{(i)}(t)$
and $P_{ij \to \kappa \ell}^{conv}$ introduced in Chapter II are calculated and discussed
for the special case of constant velocity linear trajectories. Inves-
tigation of $\frac{d}{dt}\left[P_{ij \to \kappa \ell}^{conv} \right]$ indicates that the distance of closest
approach in an encounter is an unlikely place for the inelastic trans-
fer to occur.

3.1 The Isolated Molecule Wave Functions and the Intermolecular
Potential.

a) The wave functions.

Consider a diatomic molecule with atoms of mass m_1 and m_2
separated by a distance d . Suppose that at the center of mass of

the molecule there is an ideal electric dipole   p   oriented parallel
to the molecular axis.

If d is held fixed, the solutions of Eq. 2. 1-2 describing the
motion of the molecule relative to its own mass center are simply
the rigid rotator wave functions and energy levels[1]. Thus for
molecule a,

$$\mu_a^i = Y_{j_a}^{m_a}(\theta_a, \varphi_a) \qquad (3.1\text{-}1)$$

and

$$E_a^i = j_a(j_a+1)\frac{\hbar^2}{2I} \qquad (3.1\text{-}2)$$

and similarly for molecule b.   Here I is the moment of inertia,
which in terms of the reduced mass μ is given by

$$I = \mu d^2 = \frac{m_1 m_2}{m_1 + m_2} d^2 \qquad (3.1\text{-}3)$$

and the $Y_{j_a}^{m_a}(\theta_a, \varphi_a)$ are the spherical harmonics defined as[2]

$$Y_j^m(\theta, \varphi) = i^{|m|-m}\sqrt{\frac{(2j+1)(j-|m|)!}{4\pi(j+|m|)!}}\, P_j^m(\cos\theta)\, e^{im\varphi}$$

The $P_j^m(x)$ are the associated Legendre functions, given by

$$P_j^m = \frac{(-1)^j}{2^j j!}(1-x^2)^{\frac{|m|}{2}}\frac{d^{j+|m|}}{dx^{j+|m|}}(1-x^2)^j$$

b)   The potential energy of interaction.

The energy of interaction between two ideal dipoles of strength

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1.   For an example of the quantum mechanical solution of the
     motion of a rigid rotator, see for example, H. Eyring,
     J. Walter, and G. Kimball, loc. cit., p. 72.

2.   This definition is taken from MTGL, p. 905.

$\underline{p}_a$ and $\underline{p}_b$ is given in vector form by[3]

$$\Phi_{dip} = \frac{\underline{p}_a \cdot \underline{p}_b}{|\underline{R}_{ab}|^3} - 3 \frac{(\underline{p}_a \cdot \underline{R}_{ab})(\underline{p}_b \cdot \underline{R}_{ab})}{|\underline{R}_{ab}|^5} \qquad (3.1\text{-}4)$$

In a coordinate system in which the line connecting the mass centers of the two molecules is taken as the polar axis, so that θ_a and θ_b are polar angles giving the inclination of molecules a and b relative to this axis, and φ_a and φ_b the azimuthal angles about this line, Φ_{dip} takes the special form

$$\Phi_{dip} = \frac{|\underline{p}_a||\underline{p}_b|}{|\underline{R}_{ab}|^3}\left[\sin\theta_a \sin\theta_b \cos(\varphi_a - \varphi_b) - 2\cos\theta_a \cos\theta_b \right] \qquad (3.1\text{-}4b)$$

The total energy of interaction between polar molecules may be described approximately by the Stockmayer potential[4]

$$\Phi_{ab}(\underline{r}_a, \underline{r}_b, \underline{R}_{ab}) = 4\epsilon\left[\left(\frac{\sigma}{|\underline{R}_{ab}|}\right)^{12} - \left(\frac{\sigma}{|\underline{R}_{ab}|}\right)^6 \right] \qquad (3.1\text{-}5)$$

$$+ \frac{\underline{p}_a \cdot \underline{p}_b}{|\underline{R}_{ab}|^3} - 3\frac{(\underline{p}_a \cdot \underline{R}_{ab})(\underline{p}_b \cdot \underline{R}_{ab})}{|\underline{R}_{ab}|^5}$$

The first bracketed term in this potential is a Lennard-Jones type spherically symmetric potential describing the hard core repulsive energy and the attractive dispersion energy. The remainder is just the dipole-dipole interaction energy. The constants σ and ϵ are characteristic of each molecule and are determined experimentally.

The molecular constants for HCl which will be used in subsequent calculations are as follows[5]:

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3. MTGL, p. 851.

4. W. H. Stockmayer, J. Chem. Phys. 9, 398, (1941).

5. The values of I and μ are taken from G. Herzberg, Spectra of Diatomic Molecules, Van Nostrand, 1950, p. 534. Those of $\underline{p}$, $\left[\frac{\epsilon}{k}\right]_{L.J.}$ and $[\sigma]_{L.J.}$ are from MTGL, p. 1112.

$$I = 2.6422 \times 10^{-40} \text{ gm. cm.}^2$$

$$\mathcal{H} = 1.62645 \times 10^{-24} \text{ gm.}$$

$$p = 1.034 \times 10^{-18} \text{ e.s.u.}$$

$$[\sigma]_{L.J.} = 3.305 \times 10^{-8} \text{ cm.}$$

$$\left[\frac{\epsilon}{k}\right]_{L.J.} = 360 \,^{\circ}K$$

(3.1-6)

Here $[\epsilon/k]_{L.J.}$ and $[\sigma]_{L.J.}$ are constants obtained by fitting viscosity data to the Lennard-Jones potential, and would not be expected to be precisely the same as the constants obtained by fitting equation of state data to the Stockmayer potential. Since Stockmayer constants are not available for HCl the L. J. values will be used as a rough estimate of the spherically symmetric potential.

3.2 The Effective Potential

It is not possible to solve Equ. 2.1-3 exactly for the adiabatic clamped wave functions ψ_{in}^{ci} and the effective potential $\varphi^{ci}(R_{ab})$. London[6], however, has obtained approximate solutions of the problem which allow us to construct approximate effective potentials which depend only on the distance of separation $|R_{ab}|$. London used a modified perturbation method which he called the method of unsharp resonance, but the solution is equally well viewed as a variation method.

When the molecules are far separated the wave function of the

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6.   F. London,   Z. Physik, 63, 245 (1930).

system may be written as a product of spherical harmonics

$$\Psi^o_{(j_a, m_a; j_b, m_b)} = \psi^o_o = Y^{m_a}_{j_a}(\theta_a, \varphi_a) \, Y^{m_b}_{j_b}(\theta_b, \varphi_b) \qquad (3.2\text{-}1)$$

For convenience we write this function for the initial state ψ^o_o where the superscript denotes that it is an unperturbed function, and the subscript stands for the four quantum numbers j_a, m_a, j_b, and m_b. For a trial function, London forms a linear combination of ψ^o_o and the twelve (at most) unperturbed functions with which it combines in the sense that

$$(\psi^o_i \mid \Phi_{dip} \mid \psi^o_o) \neq 0$$

These twelve functions are

$$\psi^o_1 = \psi^o_{(j_a+1, m_a; j_b+1, m_b)} \qquad\qquad \psi^o_7 = \psi^o_{(j_a+1, m_a; j_b-1, m_b)}$$

$$\psi^o_2 = \psi^o_{(j_a+1, m_a+1; j_b+1, m_b-1)} \qquad \psi^o_8 = \psi^o_{(j_a+1, m_a+1; j_b-1, m_b-1)}$$

$$\psi^o_3 = \psi^o_{(j_a+1, m_a-1; j_b+1, m_b+1)} \qquad \psi^o_9 = \psi^o_{(j_a+1, m_a-1; j_b-1, m_b+1)} \qquad (3.2\text{-}2)$$

$$\psi^o_4 = \psi^o_{(j_a-1, m_a; j_b-1, m_b)} \qquad\qquad \psi^o_{10} = \psi_o{(j_a-1, m_a; j_b+1, m_b)}$$

$$\psi^o_5 = \psi^o_{(j_a-1, m_a+1; j_b-1, m_b-1)} \qquad \psi^o_{11} = \psi_o{(j_a-1, m_a-1; j_b+1, m_b-1)}$$

$$\psi^o_6 = \psi^o_{(j_a-1, m_a-1; j_b-1, m_b+1)} \qquad \psi^o_{12} = \psi_o{(j_a-1, m_a-1; j_b+1, m_b+1)}$$

Functions with negative j values or values of $|m|$ greater than the corresponding j are taken to be zero.

The best value of the energy obtainable from this linear combination is given by solution of the 13'th order secular equation

$$\left| (\psi^o_i \mid \Phi_{dip} \mid \psi^o_j) + (E^o_i - E^o_o - \varphi) \delta_{ij} \right| = 0 \qquad (3.2\text{-}3)$$

$$i, j = 0, 1, \cdots 12$$

Here the E^o_i are the energies corresponding to the unperturbed wave functions ψ^o_i. If relative coordinates are chosen so that the intermolecular axis is taken as the z direction, the secular determinant takes on a relatively simple form. All matrix elements

vanish except those in the first row and the first column, and the diagonal elements become equal in groups of three. London shows that the secular equation may be reduced to the fifth order equation

$$\frac{|R_{ab}|^6}{\rho_a^2 \rho_b^2} \varphi = \frac{a_1^2}{\varphi - \epsilon_1} + \frac{a_2^2}{\varphi - \epsilon_2} + \frac{a_3^2}{\varphi - \epsilon_3} + \frac{a_4^2}{\varphi - \epsilon_3} \qquad (3.2\text{-}4)$$

Here the ϵ_i are given by

$$\epsilon_1 = \hbar^2 \left[\frac{j_a + 1}{I_a} + \frac{j_b + 1}{I_b} \right] \qquad \epsilon_3 = \hbar^2 \left[\frac{j_a + 1}{I_a} - \frac{j_b}{I_b} \right] \qquad (3.2\text{-}5)$$

$$\epsilon_2 = \hbar^2 \left[\frac{-j_a}{I_a} - \frac{j_b}{I_b} \right] \qquad \epsilon_4 = \hbar^2 \left[\frac{-j_a}{I_a} + \frac{j_b + 1}{I_b} \right]$$

and

$$a_i^2 = \left(\psi_{3i}^0 \,|\, \Phi_{dip} \,|\, \psi_0^0 \right)^2 + \left(\psi_{3i-1}^0 \,|\, \Phi_{dip} \,|\, \psi_0^0 \right)^2 + \left(\psi_{3i-2}^0 \,|\, \Phi_{dip} \,|\, \psi_0^0 \right)^2 \qquad (3.2\text{-}6)$$

The a_i are given explicitly in terms of the quantum numbers in MTGL[7]. For example, the coefficient a_4 is given by

$$a_4^2(j_a, m_a; j_b, m_b) = \frac{\left[\begin{array}{l} 4 \left[j_a^2 - m_a^2 \right] \left[(j_b+1)^2 - m_b^2 \right] \\ + \frac{1}{4} (j_a + m_a)(j_a + m_a - 1)(j_b + m_b + 1)(j_b + m_b + 2) \\ + \frac{1}{4} (j_a - m_a)(j_a - m_a - 1)(j_b - m_b + 1)(j_b - m_b + 2) \end{array} \right]}{\left[4 j_a^2 - 1 \right] \left[4(j_b+1)^2 \right]} \qquad (3.2\text{-}6b)$$

The solutions of Eq. 3.2-3 fall into two general classes, categorized according to their behavior for large values of R_{ab}. For non resonance interactions ($j_a \neq j_b \pm 1$) the physically significant solution is negative and is proportional to $1/R_{ab}^6$. It is shown in MTGL that the coefficient of this term is given by

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7. MTGL p. 1000.

$$\varphi_{\text{non res}}^{(R_{ab} \to \infty)} = \frac{-B_{\text{non res}}}{|R_{ab}|^6} = -\frac{p_a^2 p_b^2}{|R_{ab}|^6}\left[\frac{a_1^2}{\epsilon_1} + \frac{a_2^2}{\epsilon_2} + \frac{a_3^2}{\epsilon_3} + \frac{a_4^2}{\epsilon_4}\right] \qquad (3.2\text{-}7)$$

For resonant interactions $(j_a = j_b \pm 1$, and $p_a = p_b = p)$ there are two solutions of Eq. 3.2-3 which for large R_{ab} differ only in sign and are proportional to $1/R_{ab}^3$. In MTGL the coefficients are given as

$$\varphi_{\text{res}}(R_{ab} \to \infty) = \pm a_4 \frac{p^2}{|R_{ab}|^3} \qquad (3.2\text{-}8)$$

Solutions of Eq. 3.2-3 for these two cases are tabulated in Table 3.2-1 and are plotted in Fig. 3.2-1, for the interaction of two HCl molecules. Curve A gives the non resonant interaction when both molecules are in their ground states. The pair of curves labeled B give the interaction energy for the resonant case $j_a = 1$, $m_a = 0$; $j_b = 2$, $m_b = 1$. The pair labeled C are for the resonant case $j_a = 2$, $m_a = 0$; $j_b = 3$, $m_b = 3$. For comparison, curve D gives the attractive part of the Lennard-Jones potential, which is proportional to $1/R_{ab}^6$. Molecular constants are taken from Eq. 3.1-6.
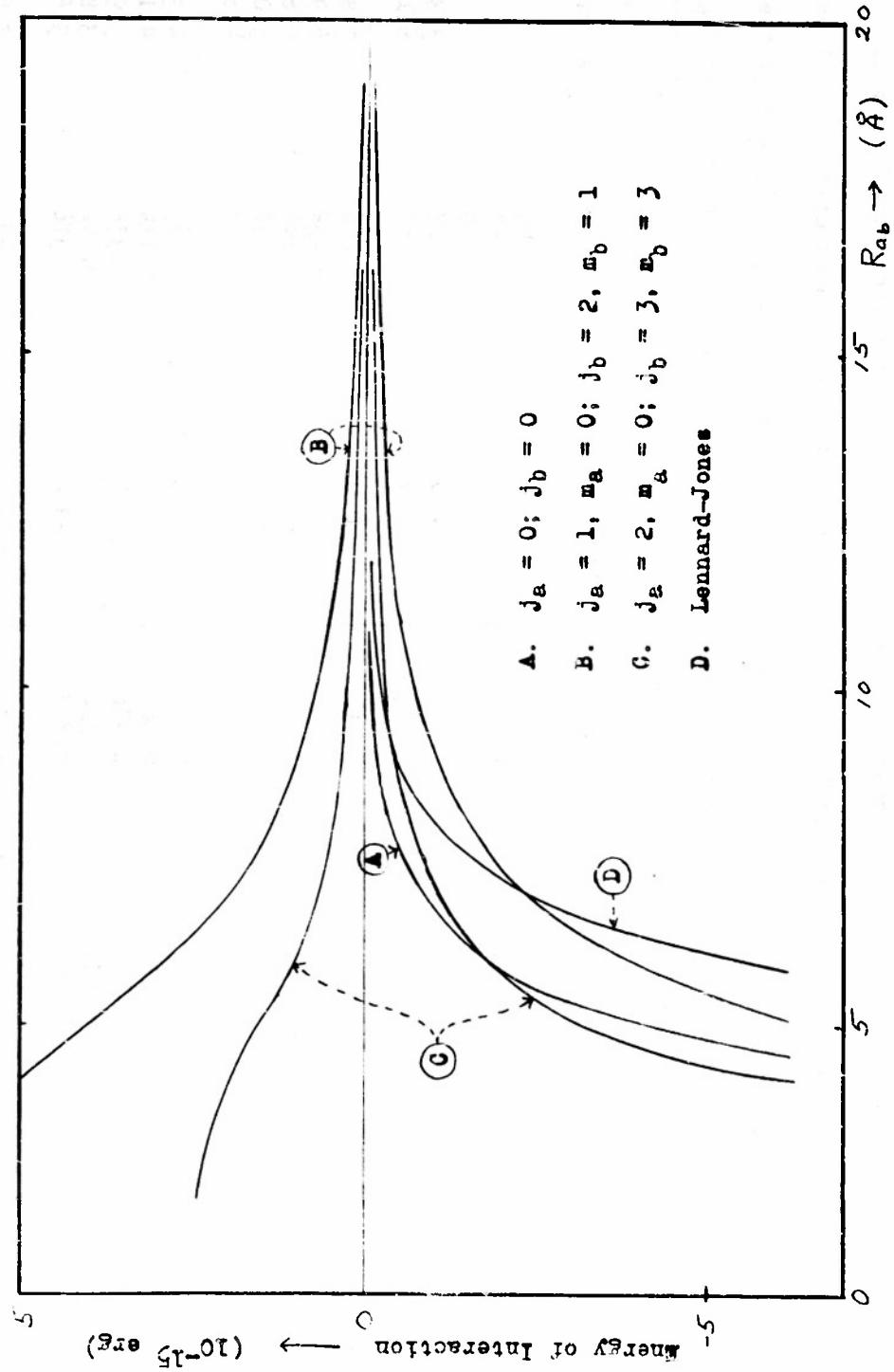
Fig. 2.3-1 The interaction energy of rotating linear dipoles

held at a fixed separation R_{ab}. plotted as a function of R_{ab}.

Legend within figure:

A. $j_a = 0$; $j_b = 0$

B. $j_a = 1$, $m_a = 0$; $j_b = 2$, $m_b = 1$

C. $j_a = 2$, $m_a = 0$; $j_b = 3$, $m_b = 3$

D. Lennard-Jones

Axes: Energy of Interaction (10^{-15} erg), $R_{ab} \rightarrow$ (Å)

Table 3.2-1

The Interaction Energy of Rotating Linear Dipoles Held at a Fixed Separation R_{ab}.

For case A ($j_a = 0$; $j_b = 0$) and case D (Lennard-Jones) the energy is calculated for various R_{ab}.

For case B ($j_a = 1$, $m_a = 0$; $j_b = 2$, $m_b = 1$) and case C ($j_a = 2$, $m_a = 0$; $j_b = 3$, $m_b = 3$) the separation corresponding to various interaction energies is calculated. Results are plotted in Fig. 2.3-1.

R (Angstroms)	E_A (10^{-15} erg)	E_D (10^{-15} erg)	E (10^{-15} erg)	$(R_{ab})_B$ (Angstroms)	$(R_{ab})_C$ (Angstroms)
3.0	-28.5	280.0	5.0	4.149	
3.5	-16.7	-41.0	4.0	4.967	
4.0	-10.1	-43.0	3.0	5.760	
4.5	-6.31	-26.3	2.0	6.813	3.875
5.0	-3.99	-15.2	1.0	8.782	6.128
5.5	-2.55	-8.91	0.05	11.166	7.846
6.0	-1.65	-5.40	-1.0	9.052	6.913
6.5	-1.08	-3.37	-2.0	7.261	5.849
7.0	-0.724	-2.18	-3.0	6.398	5.040
7.5	-0.491	-1.44	-4.0	5.855	4.652
8.0	-0.339	-0.983	-5.0	5.469	4.373
8.5	-0.239	-0.684	-6.0	5.174	4.156
9.0	-0.171	-0.486	-7.0	4.938	3.978
9.5	-0.124	-0.352	-8.0	4.742	3.828
10.0	-0.0916	-0.259	-9.0	4.576	3.697
10.5	-0.0685	-0.193	-10.0	4.432	3.581
11.0	-0.0520	-0.146	-11.0	4.306	3.474
11.5	-0.0398	-0.112	-12.0	4.194	3.375
12.0	-0.0310	-0.087			

a) Non Resonant Interactions

The non resonant interactions are best examined by looking at the coefficient of the $1/R_{ab}^6$ term which describes the interaction at large separations. The constant $B_{nm\,res}$ for several sets of quantum numbers, and for R_{ab} measured in units of 10^{-8} cm. , is given in Table 3.2-2.

Table 3.2-2

Coefficients of the interaction energy term proportional to $1/R_{ab}^6$ in non resonant collisions

Internal states	$B_{nm\,res}$ $[erg\ \AA^6]$
$j_a = 0$, $m_a = 0$; $j_b = 0$, $m_b = 0$	9.06×10^{-11}
$j_a = 5$, $m_a = 2$; $j_b = 5$, $m_b = 2$	1.12×10^{-10}
$j_a = 10$, $m_a = 0$; $j_b = 10$, $m_b = 0$	1.34×10^{-10}
$j_a = 5$, $m_a = 0$; $j_b = 10$, $m_b = 0$	6.04×10^{-12}

This may be compared to the coefficient of the term in the Lennard-Jones potential which varies as $1/R_{ab}^6$,

$$B_{LJ} = 4\epsilon\sigma^6$$

For the values given in Eq. 3.1-6 for HCl, $B_{LJ} = 2.59 \times 10^{-10}\ erg\ \AA^6$

Since B_{LJ} represents some sort of an average of the dispersion energy and the various dipole-dipole forces, it appears likely that the dispersion energy is at least of the same order of magnitude as

the various non resonance dipole-dipole forces. London[8] investigates this question in detail for several polar gases, and concludes that none of the forces between HCl molecules which arise directly from the electric dipoles are as large as the dispersion force.

b) Resonant interactions.

The resonant interactions are of particular interest, and are best investigated by looking at the coefficient a_4 (Eq. 3.2-6b). First, however, note by comparison with Eq. 3.1-4b for the static interaction of two dipoles, that a_4 represents some sort of an average over the angular factor

$$\sin\theta_a \sin\theta_b \cos(\varphi_a - \varphi_b) - 2\cos\theta_a \cos\theta_b$$

which gives the orientation of the dipoles relative to the intermolecular axis. The absolute value of this factor varies from a maximum of two when the molecules are parallel $(\theta_a = 0, \pi ; \theta_b = 0, \pi)$ to a minimum of zero when they are perpendicular $(\theta_a = \theta_b = \frac{\pi}{2})$. Hence we expect a_4 to lie somewhere in this range. For some typical resonant interactions a_4 has the values given in Table 3.2-3.

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8. F. London, Trans. Faraday Soc., <u>189</u>, 8 (1937)

Table 3.2-3

London Factor for the Coefficient of the Interaction
Energy Term Proportional to $1/R_{ab}^3$ in resonant
Collisions.

Internal states	a_4
$j_a = 1,\ m_a = 0;\ j_b = 2,\ m_b = 1$	0.586
$j_a = 1,\ m_a = 0;\ j_b = 2,\ m_b = 2$	0.436
$j_a = 1,\ m_a = 0;\ j_b = 2,\ m_b = -1$	0.169
$j_a = 4,\ m_a = 0;\ j_b = 5,\ m_b = 0$	0.531

Apparently the averaged dipole-dipole energy is of the order of 25%
or less of the maximum interaction energy of the static dipoles.

Krieger[9] performed a very interesting calculation of the viscosity
of polar gases, by using a spherically symmetric potential function
related to the Stockmayer potential. He assumed that the energy of
interaction between polar molecules could be expressed in the form

$$\Phi_{ab} = 4\epsilon\left[\left(\frac{\sigma}{R_{ab}}\right)^{12} - \left(\frac{\sigma}{R_{ab}}\right)^{6}\right] - 2\frac{p^2}{R_{ab}^3}$$

Here p is the experimental value of the dipole moment, and σ
and ϵ are adjustable constants used to fit the experimental data.
This potential energy function corresponds to the Stockmayer poten-
tial when the dipoles are oriented in the parallel orientation of minimum
energy, as in the accompanying diagram.

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9.   F. J. Krieger, Project Rand Report RM-646 (1951).
      See also MTGL p. 597.

$$\longleftarrow R_{ab} \longrightarrow$$

For this orientation the angular factor of the Stockmayer potential (Eq. 3.1-4b) is equal to minus two.

Although this theory ignores the effects of the internal degrees of freedom, Krieger is able to fit the experimental viscosity data of polar gases over the entire experimental temperature range to within experimental error. This surprising success might be interpreted as follows:

1. An appreciable fraction of the collisions in a gas of rigid rotators are resonant collisions. $(j_b = j_a \pm 1)$ The fraction of resonant collisions, f_{res} is given by

$$f_{res} = \frac{3 e^{-\frac{\hbar^2}{I k T}} + \sum_{j=1}^{\infty} (2j+1) e^{-j(j+1)\frac{\hbar^2}{2I\hbar T}} \left[(2j-1) e^{-j(j-1)\frac{\hbar^2}{2Ik T}} + (2j+3) e^{-(j+1)(j+3)\frac{\hbar^2}{2Ik T}} \right]}{\left[\sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\frac{\hbar^2}{2Ik T}} \right]^2}$$

(3.2-9)

$$= \frac{2 \sum_{j=0}^{\infty} (2j+1)(2j+3) e^{-2(j+1)^2 \frac{\hbar^2}{2Ik T}}}{\left[\sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\frac{\hbar^2}{2Ik T}} \right]^2}$$

For large values of I and T this may be evaluated by replacing the sums by integrals. In this case

$$f_{res} = \sqrt{\frac{\pi}{2}} \sqrt{\frac{\hbar^2}{2Ik T}}$$

(3.2-9a)

For collisions between HCl molecules at 300° K., this gives

$$f_{res} = .283$$

2. In resonant collisions the translational energy is conserved, so that the collision is sort of a quasi elastic collision. In Eq. 1.2-2 for the Uhlenbeck form of the viscosity coefficient the term multiplied by the net change of internal energy ΔE_{1j}^{kl} vanishes, and the

property we average over all possible encounters is just

$$g^4 \left[1 - \cos^2 \chi \right]$$

as in the expression for spherical molecules, Eq. 1.2-1.

3. Apparently the quasi elastic resonant encounters are of such importance in viscosity that Krieger was able to predict the essential behavior of the gas simply by including the long range energy term proportional to $1/R_{ab}^3$. We have seen that in all non resonant interactions the coefficient of this term should be zero, and that in resonant collisions it should depend on the quantum states of the colliding molecules. In resonant collisions, moreover, it should be considerably smaller than Krieger's value of $2\mathcal{P}^2$, and should be repulsive in some collisions, and attractive in others. Adjustment of the coefficients σ and ϵ in Krieger's theory is able to compensate for all of these approximations.

Although these considerations have been in terms of our study of linear molecules, whereas Krieger's measurements included non linear molecules, the general behavior would be expected to be the same. Margenau[10] and Warren have investigated the first order interactions of ideal dipoles imbedded in symmetric tops, and find interactions proportional $1/R_{ab}^3$ even in the non resonant cases.

c) Suggested procedure for considering the viscosity of polar gases.

From the considerations in this section, of the effective intermolecular potential arising between linear molecules containing electric dipoles, we would suggest the following procedure for predicting the viscosity of gases composed of such molecules:

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10. H. Margenau and D. T. Warren, Phys. Rev., 51, 748 (1937)
See also MTGL, p. 1004.

Consider the gas as a mixture, with each set of rotational quantum numbers defining a separate molecular species. The fraction of the molecules which are of species a specified by the rotational quantum numbers j_a and m_a is given at thermal equilibrium by

$$f_a = \frac{e^{-j_a(j_a+1)\frac{\hbar^2}{2I k T}}}{\sum_{\ell=0}^{\infty}(2\ell+1)\, e^{-\ell(\ell+1)\frac{\hbar^2}{2I k T}}} \tag{3.2-10}$$

When two molecules of species a and b collide such that $j_a \neq j_b \pm 1$ the dynamics of the encounter are determined by the inter-molecular potential function.

$$\varphi = 4\epsilon\left[\left(\frac{\sigma}{R_{ab}}\right)^{12} - \left(\frac{\sigma}{R_{ab}}\right)^{6}\right] \tag{3.2-11}$$

Where σ and ϵ are experimental constants determined by fitting experimental values of the second virial coefficient as a function of temperature to the Stockmayer potential (Eq. 3.1-5). The fraction of the collisions in the gas which are governed by this potential is $(1 - f_{res})$ where f_{res} is given by Eq. 3.2-9a.

When species a and b are such that $j_a = j_b \pm 1$, the potential energy of interaction is taken to be of form

$$\varphi = 4\epsilon\left[\left(\frac{\sigma}{R_{ab}}\right)^{12} - \left(\frac{\sigma}{R_{ab}}\right)^{6}\right] + \xi\,\frac{p^2}{R_{ab}^3} \tag{3.2-12}$$

here p is the experimental value of the dipole moment, and the quantity ξ is related to the quantities a_4 defined in Eq. 3.2-6b.

Let us call a collision in which either of the molecules is in state a and the other in state b an a-b collision. If we label our molecules such that $j_a = j_b + 1$, then in half of the a-b collisions we take

$$\xi(j_a, m_a; j_b, m_b) = + a_4(j_a, m_a, j_b, m_b)$$

and in the other half

$$\xi(j_a, m_a, j_b, m_b) = -a_y(j_a, m_a; j_b, m_b)$$

The fraction of the collisions in the gas which are a-b collisions is just $2f_a f_b$, where the factor of two results from the fact that either molecule may be in the higher energy state.

The dynamics of encounters governed by the Lennard-Jones type potential of Eq. 3.2-11 have been calculated and tabulated.[11] The dynamics of collisions governed by the potential of Eq. 3.2-12 are given in Krieger's work[8], for negative values of ξ. If Krieger's calculations were extended to include positive values of ξ it would not be a difficult matter to test this theory of the viscosity of linear polar molecules.

The viscosity of symmetric top molecules with imbedded electric dipoles could be calculated in a manner very similar to this, using the effective potentials calculated by Margenau and Warren[9]. The chief difference would be that a larger fraction of the encounters would be governed by potentials which contained a term proportional to $1/R_{ab}^3$.

3.3 The Probability of Transition

a)   Comparison of $P_{ij \to \kappa\ell}^{(o)}(t)$, $P_{ij \to \kappa\ell}^{(i)}(t)$ and $P_{ij \to \kappa\ell}^{class}(t)$.

The three transition probabilities introduced in Chapter II were

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11. MTGL p. 1132.

$$P^{(c)}_{i,j \to \kappa \ell}(t) = \left| \frac{1}{i\hbar} \int_{-\infty}^{t} e^{-\frac{i}{\hbar}[E_a^i + E_b^j - E_c^\kappa - E_b^\ell]t'} (\mu_a^\kappa \mu_b^\ell | \Phi_{ab} | \mu_a^i \mu_b^j) \, dt' \right|^2 \tag{2.2-1}$$

$$P^{(1)}_{i,j \to \kappa \ell}(t) = \left| \int_{-\infty}^{t} \frac{e^{-\frac{i}{\hbar} \int_0^{t'} \{E_{int}^{ij}[R_{ab}(\theta)] - E_{int}^{\kappa\ell}[R_{ab}(\theta)]\} d\theta}}{E_{int}^{ij}[R_{ab}(t')] - E_{int}^{\kappa\ell}[R_{ab}(t')]} (\psi_{int}^{\kappa\ell} | \frac{d\Phi_{ab}}{dt'} | \psi_{int}^{ij}) \, dt' \right|^2 \tag{2.2-2}$$

and

$$P^{class}_{i,j \to \kappa \ell}(t) = \frac{\int_{-\infty}^{t} (\psi_{int}^{\kappa\ell} | \frac{d\Phi_{ab}}{dt'} | \psi_{int}^{ij})^2 | \frac{dR}{dt'} |^{-1} dt'}{\int_{-\infty}^{\infty} (\psi_{int}^{\kappa\ell} | \frac{d\Phi_{ab}}{dt'} | \psi_{int}^{ij})^2 | \frac{dR}{dt'} |^{-1} dt'} P^{(1)}_{i,j \to \kappa \ell}(\infty) \tag{2.2-6}$$

Here $P^o_{i,j \to \kappa \ell}(t)$ was derived from a time dependent perturbation procedure in which the unperturbed functions were taken to be simple products of the isolated molecule wave functions $\mu_a^i(\theta)$ and $\mu_b^j(\theta)$. $P^{(1)}_{i,j \to \kappa \ell}(t)$ was obtained by using the adiabatic clamped functions $\psi_{int}^{ij}(\theta,\theta,R_{ab})$ as a time dependent unperturbed set. The function $P^{class}_{i,j \to \kappa \ell}(t)$ was suggested in Sec. 2.2 as a semi-classical analogue of $P^{(1)}_{i,j \to \kappa \ell}(t)$.

In order to better understand these three functions, we calculate each of them for the special case in which the equivalent one particle trajectory is a straight line traversed at constant velocity (Fig. 3.3-1) Although this approximation would not in general be valid if we were seeking precise numerical results, it will be adequate for illustrating and comparing the general behavior of these functions. The advantage of the approximation is that the time dependence of the matrix elements of Φ_{ab}, originating in the factor $1/R_{ab}^3$ now appears simply as $[b^2 + j^2 t'^2]^{-3/2}$.

For the purpose of these approximate calculations we also replace the adiabatic clamped functions ψ_{int}^{ij} and
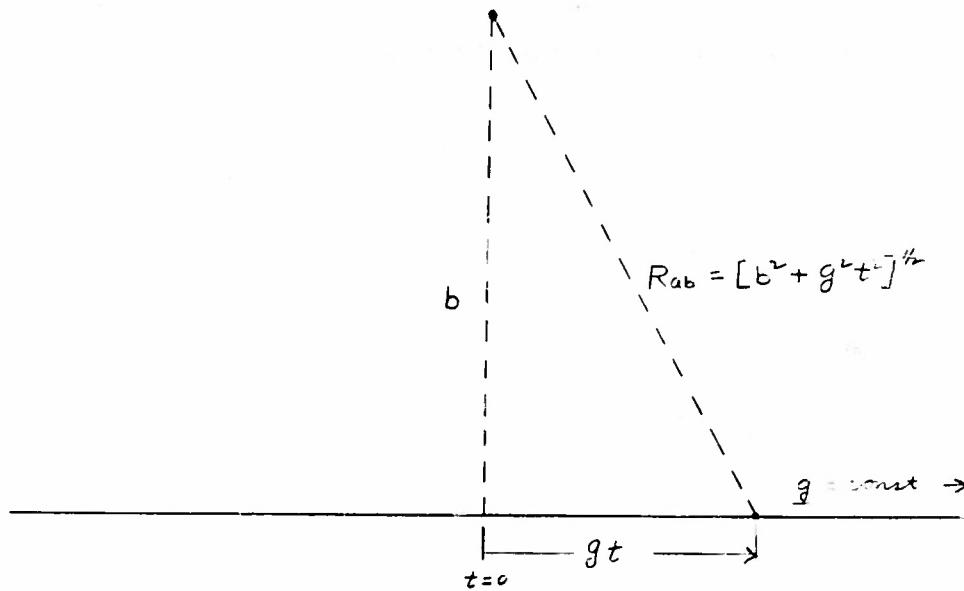
Fig. 3.3-1   The simplest case of an
equivalent one particle trajectory.

energies $E_{int}^{ij}(R_{ab})$ by their zero order approximations $\mu_a^i \mu_b^j$
and $E_a^i + E_b^j$.

With these approximations, the transition probabilities may be
written

$$P_{ij \to kl}^{(o)}{}_{(t)} = \left[K_{ij}^{kl} \int_{-\infty}^{y} \frac{e^{-iy}}{[c^2 + y^2]^{3/2}} \, dy \right]^2 \tag{3.3-1}$$

$$P_{ij \to kl}^{(1)}{}_{(t)} = \left[3 K_{ij}^{kl} \int_{-\infty}^{y} \frac{y \, e^{-iy}}{[c^2 + y^2]^{5/2}} \, dy \right]^2 \tag{3.3-2}$$

$$P_{i j \to \kappa \ell}^{class}(t) = \frac{7}{2} \int_{-\infty}^{z} \frac{|z| \, dz}{[1+z^2]^{3/2}} \, P_{i j \to \kappa \ell}^{(i)}(\infty) \qquad (3.3-3)$$

The various quantities appearing here are as follows:

$$y = \frac{E_a^\kappa + E_b^\ell - E_a^i - E_b^j}{\hbar} \, t = \frac{\Delta E_{ij}^{\kappa \ell}}{\hbar} \, t$$

$$z = \frac{g \cdot t}{b}$$

$$c = \frac{b \, \Delta E_{ij}^{\kappa \ell}}{\hbar \, g}$$

$$K_{ij}^{\kappa \ell} = \alpha_{ij}^{\kappa \ell} \left(\frac{p_a \, p_b}{\Delta E_{ij}^{\kappa \ell}} \right) \left(\frac{\Delta E_{ij}^{\kappa \ell}}{\hbar \, g} \right)^3$$

$$\alpha_{ij}^{\kappa \ell} = \frac{\kappa_{ab}^3}{p_a \, p_b} \left(\mu_a^\kappa \mu_b^\ell \, | \, \Phi_{dip} \, | \, \mu_a^i \mu_b^j \right)$$

$$= \int_0^\eta d\theta_a \int_0^{2\eta} d\varphi_a \int_0^\eta d\theta_b \int_0^{2\pi} d\varphi_b \, Y_{\lambda_a}^{\mu_a}(\theta_a, \varphi_a) \, Y_{\lambda_b}^{\mu_b}(\theta_b, \varphi_b) \left[\begin{array}{c} \sin\theta_a \sin\theta_b \cos(\varphi_a - \varphi_b) \\ - 2 \cos\theta_a \cos\theta_b \end{array} \right] Y_{j_a}^{m_a}(\theta_a, \varphi_a) \, Y_{j_b}^{m_b}(\theta_b, \varphi_b)$$

Here the quantum numbers abbreviated by ij, and kl are

$$i \sim j_a, \, m_a \qquad \kappa \sim \lambda_a, \, \mu_a$$
$$j \sim j_b, \, m_b \qquad \ell \sim \lambda_b, \, \mu_b$$

We also use the result that[12]

$$\int_{-\infty}^\infty \frac{e^{-iy}}{[c^2 + y^2]^{3/2}} \, dy = -\frac{\pi}{c} \, H_1^{(1)}(ic)$$

Where $H_1^{(1)}$ is the first order Hankel function of the first kind, tabulated in Jahnke and Emde[13]. The integrals $\alpha_{ij}^{\kappa \ell}$

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12. G.N. Watson, A Treatise on the Theory of Bessel Functions Camb. Univ. Press, Second ed. p. 172.

13. E. Jahnke and F. Emde, Tables of Functions, Dover, 1945, p. 133.

may be calculated directly from the properties of spherical harmonics or they may be found listed in convenient form by Margenau[14].

In Table 3.3-1 and Fig. 3.3-2 we give calculated values of the three transition probabilities for the case when the initial relative velocity g (taken to be constant throughout the encounter), the collision parameter b, and the change in internal quantum states are

$$g = 3.1924 \times 10^5 \text{ cm./sec.}$$
$$b = 4.89 \times 10^{-8} \text{ cm.}$$

$$j_a = 4, \ m_a = 0; \ j_b = 3, \ m_b = 0$$

$$\lambda a = 5, \ \mathcal{H}_a = 0; \ \lambda_b = 4, \ \mathcal{H}_b = 0$$

The constants correspond to a typical encounter for HCl molecules at room temperature.

The principal deviations of $P_{i\,\to\,\kappa\ell}^{(o)}(t)$ and $P_{a\,\to\,\kappa\ell}^{\prime\prime}(t)$ from the general form of $P_{i\,\to\,\kappa\ell}^{class}(t)$ are not too difficult to understand. The oscillatory motion of these two probabilities, with period equal to $\hbar / \Delta E_{i\,j}^{\kappa\ell}$ is a typical quantum mechanical phenomenon which may be interpreted either as a diffraction effect resulting from the wave-like nature of matter, or as a consequence of the uncertainty principle. From the point of view of the uncertainty principle, we are not allowed to specify the time interval δt during which the energy change $\Delta E_{i\,j}^{\kappa\ell}$ took place more precisely than about

$$\delta t \gg \frac{\hbar}{\Delta E_{i\,j}^{\kappa\ell}}$$

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14. H. Margenau, Rev. Mod. Phys. __11__, 1 (1939).

$$A = P_{ij \to k\ell}^{(0)}(t)$$

$$B = P_{ij \to k\ell}^{(1)}(t)$$

$$C = P_{ij \to k\ell}^{class}(t)$$

$$D = \left| \frac{(\mu_a^\pi \mu_\delta^\rho | \Phi | \mu_a^\pi \mu_\delta^\rho)}{\Delta E_{ii}^{\pi i}} \right|^2$$
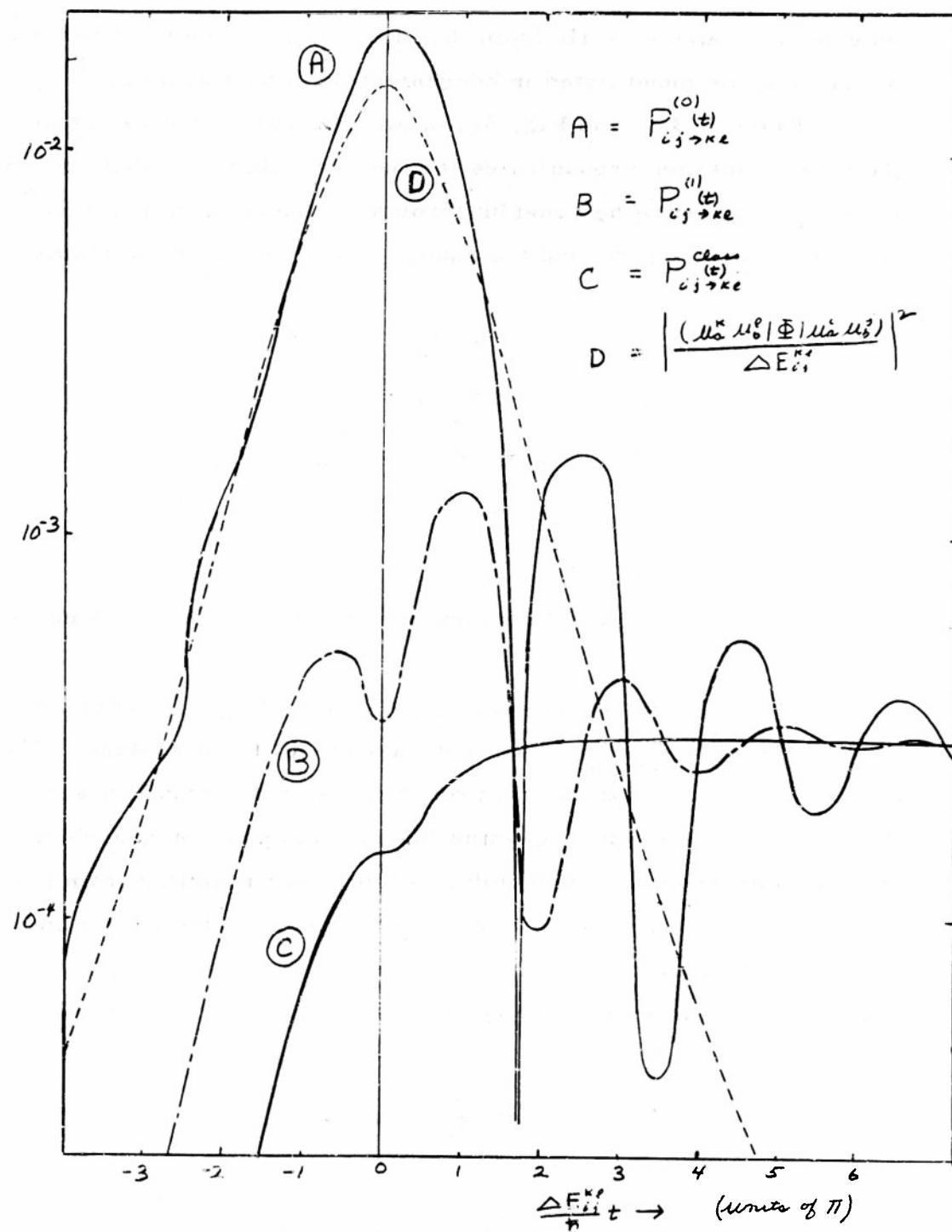
Fig. 3.3-2 Probability of a rotational
transition along a straight line trajectory

Table 3.3-1

Transition Probabilities along a Straight Line Trajectory

$\frac{\Delta E}{\hbar} \div$ (units of π)	$P^{(0)}_{ij \to k\ell}(t) \times 10^3$	$P^{(1)}_{ij \to k\ell}(t) \times 10^3$	$P^{class}_{ij \to k\ell}(t) \times 10^3$	$\left\|\frac{\langle \mu^x_a \mu^o_b \| \Phi \| \mu^i_a \mu^o_b \rangle}{\Delta E}\right\|^2 \times 10^3$
-7.0	0.0218	0.0000		0.0031
-6.5	0.0072	0.0000		0.0062
-6.0	0.0085	0.0000		0.0080
-5.5	0.0000	0.0000		0.0116
-5.0	0.0226	0.0005		0.0195
-4.5	0.0296	0.0011		0.0340
-4.0	0.0709	0.0023		0.0621
-3.5	0.142	0.0053	0.0006	0.1190
-3.0	0.205	0.0127	0.0024	0.2452
-2.5	0.497	0.0322	0.0030	0.5325
-2.0	1.16	0.0950	0.0084	1.221
-1.5	2.58	0.2078	0.0230	2.867
-1.0	5.97	0.4214	0.0625	6.409
-0.5	12.6	0.5045	0.1100	11.82
0.0	13.1	0.3344	0.1496	14.95
0.5	16.6	0.8667	0.1860	11.82
1.0	7.41	1.276	0.2423	6.409
1.5	1.21	0.6576	0.2782	2.867
2.0	1.16	0.0950	0.2877	1.221
2.5	1.51	0.268	0.2961	0.5325
3.0	0.614	0.4292	0.2967	0.2452
3.5	0.0361	0.3278	0.2985	0.1190
4.0	0.263	0.2508		0.0621
4.5	0.490	0.2909		0.0340
5.0	0.320	0.3242		0.0195
5.5	0.178	0.3037		0.0116
6.0	0.269	0.2863		0.0080
6.5	0.351	0.2972		0.0062
7.0	0.301	0.3065		0.0031
7.5	0.232	0.3003		0.0021
8.0	0.274	0.2946		0.0014
∞	0.2991	0.2991	0.2991	

This means that we are not allowed to ask about the probability of
transition during time intervals less than that corresponding to about
one cycle of the curves of Fig. 3.3-1.

The large maximum in $P_{ij \to k\ell}^{(o)}(t)$, about $t = 0$ may be understood
by noting that $P_{ij \to k\ell}^{(o)}(t)$ actually gives the transition probability for
an experiment in which the collision is allowed to proceed until
time t, that the perturbation is suddenly turned off. The sudden
turning off of the perturbation itself induces transitions, corresponding
to the fact that at that moment the true wave function of the system
has large contributions of other unperturbed states, simply because
of the adiabatic distortion. For comparison, curve D of Fig. 3.3-2
is a plot of

$$\left| \frac{(\mu_a^k \mu_b^\ell \mid \Phi_{a_{ij}} \mid \mu_a^i \mu_b^j)}{\triangle E_{ij}^{k\ell}} \right|^2$$

the first order perturbation estimate of the contribution of the kl
state to the wave function in an adiabatic encounter. This curve
accounts very well for the wide maximum in $P_{ij \to}^{(o)}(t)$.

The transition probability $P_{ij \to k\ell}^{(1)}(t)$ corresponds more nearly to
an experiment in which at time t the relative motion of the molecules
is stopped and they are separated adiabatically to infinity. The fact
that there may still be something of a maximum in the vicinity of
the point of closest approach (t = 0) may be due to the approxima-
tion of evaluating the energy and matrix elements in terms of the $\mu_a^i \mu_b^j$.

The fact that $P_{ij \to k\ell}^{(o)}(t)$ and $P_{ij \to k\ell}^{(1)}(t)$ approach the same value at
$t = \infty$ is understandable. since in this limit the adiabatic functions
become identical with the simple product functions. Mathematically
the equivalence may be demonstrated by integrating Eq. 3.3-1 by
parts; consistent with the assumptions we have made in the evaluation
of $P_{ij \to k\ell}^{(1)}(t)$, it follows immediately that $P_{ij \to k\ell}^{(o)}(\infty) = P_{ij \to k\ell}^{(1)}(\infty)$, for all
transitions.

b) Dependence of the transition probability on g, b, and $\triangle E_{ij}^{\kappa\ell}$

To show how strongly the transition probability depends on the relative velocity, g, the collision parameter, b, and the energy exchange $\triangle E_{ij}^{\kappa\ell}$, we have calculated $P_{ij \to \kappa\ell}^{(1)}(\infty)$ for collisions between HCl molecules, varying each of these quantities separately. The results are given in Table 3.3-2.

From these calculations we see that changing each of these quantities by less than a factor of two changes the total probability of transition by a factor of about one hundred. In an actual calculation of the cross sections, this would mean that the main contribution to each differential cross section would be expected to come from a relatively narrow range of relative velocities and collision parameters.

c) Location of the transition along the trajectory.

In the semi-classical theory of collisions it is necessary to know where along the trajectory a given transition has taken place. In our semi-classical description of collisions this is given by the shape of the function $P_{ij \to \kappa\ell}^{class}(t)$ or by the related function $\frac{d}{dt}\left[P_{ij \to \kappa\ell}^{class}(t)\right]$.

$P_{ij}^{class}(t)$ gives the probability that the transition has occurred up to time t, and $\frac{d}{dt}\left[P_{ij \to \kappa\ell}^{class}(t)\right]$ gives the probability that the transition occurs in the time interval dt about t. From Eq. 3.3-3 it may be seen that to the approximations used in deriving that equation, each of these is given by "shape factors" which depend only on the reduced variable, z = gt/b. Thus they may be written

$$P_{ij \to \kappa\ell}^{class}(t) = S(z)\, P_{ij \to \kappa\ell}^{(1)}(\infty) \qquad (3.3-4)$$

and

$$\frac{d}{dt}\left[P_{ij \to \kappa\ell}^{class}(t)\right] = \frac{g}{b}\, S'(z)\, P_{ij \to \kappa\ell}^{(1)}(t) \qquad (3.3-5)$$

Table 3.3-2

Dependence of the Total Transition Probability on the Relative Velocity, Collision Parameter, and Quantum Transition

	b $\overset{\circ}{A}$ngstroms	g 10^5 cm./sec.	ΔE_{ij}^{kl} 10^{-14} ergs	quantum transition*	$P_{ij \to kl}^{(1)}$
1	4.89	3.192	3.787	a	2.991×10^{-4}
2	4.00	3.192	3.787	a	4.107×10^{-3}
3	5.50	3.192	3.787	a	5.071×10^{-5}
4	4.89	2.600	3.787	a	4.360×10^{-5}
5	4.89	4.000	3.787	a	2.904×10^{-3}
6	4.89	3.192	4.208	b	4.380×10^{-5}
7	4.89	3.192	2.525	c	4.578×10^{-5}

* The changes in internal quantum numbers are as follows:

a $\left\{ \begin{array}{l} j_a: 4 \to 5 \\ m_a: 0 \to 0 \\ j_b: 3 \to 4 \\ m_b: 0 \to 0 \end{array} \right.$

b $\left\{ \begin{array}{l} j_a: 4 \to 5 \\ m_a: 0 \to 0 \\ j_b: 4 \to 5 \\ m_b: 0 \to 0 \end{array} \right.$

c $\left\{ \begin{array}{l} j_a: 2 \to 3 \\ m_a: 0 \to 0 \\ j_b: 2 \to 3 \\ m_b: 0 \to 0 \end{array} \right.$

where

$$S_{(z)} = \frac{7}{2} \int_{-\infty}^{Z} \frac{|z| \, dz}{[1 + z^4]^{9/4}}$$

and

$$S'_{(z)} = \frac{7}{2} \frac{|z|}{[1 + z^4]^{9/4}}$$

To illustrate the behavior of these functions, we give calculated values of S(z) in Table 3.3-3 and plot the results in Fig. 3.3-3. The most interesting feature of this curve is the plateau in the vicinity of t = 0, the distance of closest approach. The significance of this plateau is seen even more clearly in Fig. 3.3-4 where we plot the function S'(z). From this curve we see that the probability that the transition occurs during an infinitesimal time increment about t = 0 is zero. The maximum probability of transition occurs when $gt = b/2\sqrt{2}$.

The location of the maximum of the function $\frac{d}{dt}[P^{class}_{(t)}]$ at exactly $b/\sqrt{2}$ is of course due to our approximate form of $P^{class}_{(t)}$ but the zero at the distance of closest approach appears even in the accurate quantum mechanical formula. Thus

$$\frac{d}{dt} P^{m}_{ij+1} = \frac{(\psi^{x_i}_{int}|\Phi|\psi^{i}_{int})}{\Delta E^{x_i}_{ij}(t)} 2 \mathcal{Re} \left[e^{-\frac{t}{\hbar}\int_0^t \Delta E^{x_i}_{ij}(\theta)d\theta} \int_{-\infty}^{t} \frac{e^{\frac{i}{\hbar}\int_\infty^t \Delta E^{i}_{ij}(\theta)d\theta}}{\Delta E^{i}_{ij}(t)} \left(\psi^{x_i}_{int}|\frac{d\Phi}{dt}|\psi^{i}_{int}\right) dt' \right] \quad (3.3-6)$$

Since the distance of closest approach is a stationary point of R_{ab}, $\left(\psi^{x_i}_{int}|\frac{d\Phi}{dt}|\psi^{i}_{int}\right) = 0$ at t = 0. Thus the probability that the transition occurs in the time interval dt about the point t=0 vanishes.

One must be careful in interpreting this result, however, not to conclude that the segment of the trajectory about the distance of closest approach is always an unlikely place for a transition to occur. In

71.
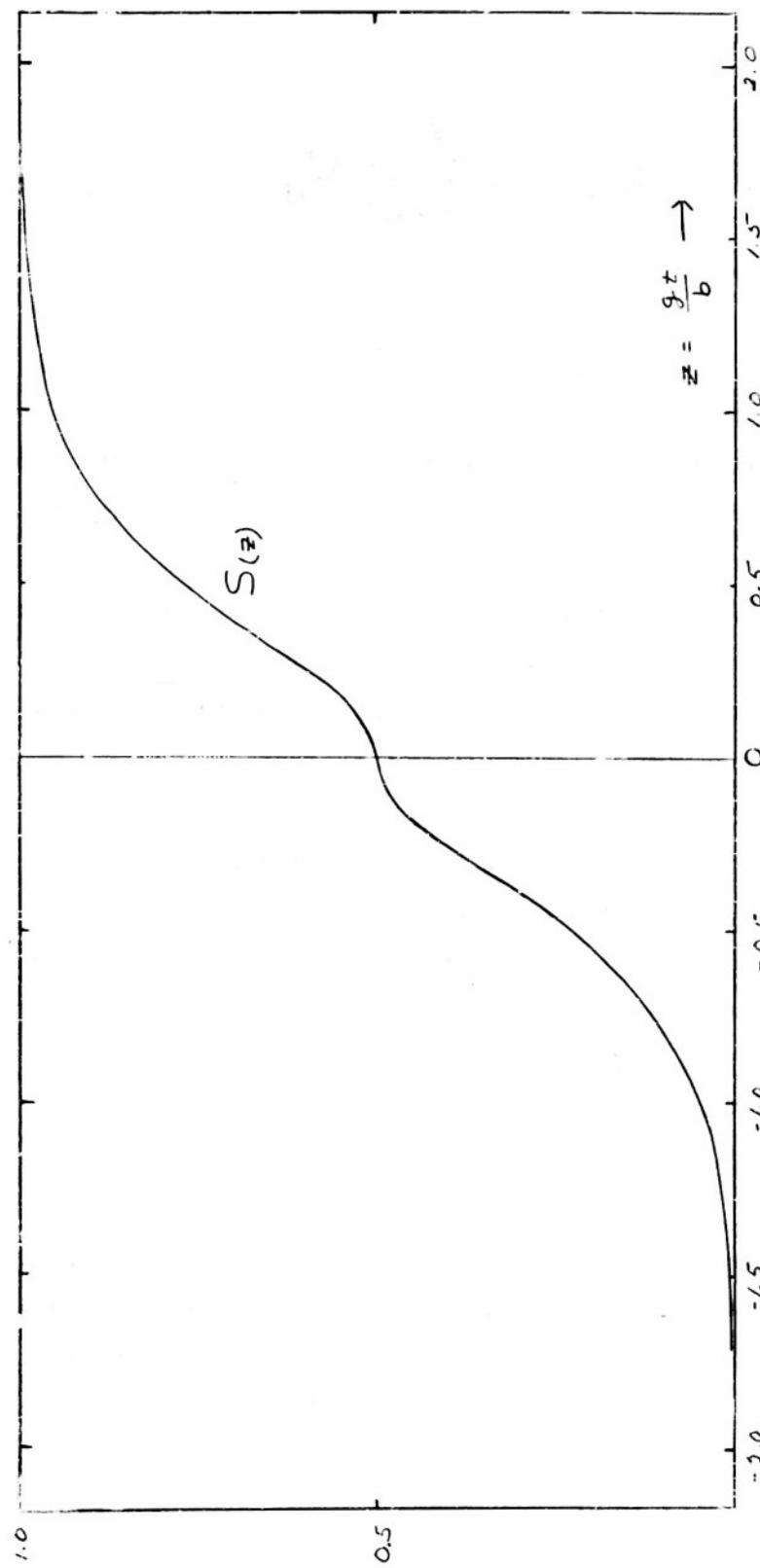
Fig. 3.3-3 The shape factor $S(z)$, defined by $P^{Clos}_{ij \to kl}{}^{(t)} = S(z) P^{(t)}_{ij \to kl}{}^{(\infty)}$, and evaluated for a straight line constant velocity trajectory where $z = \frac{gt}{b}$. $S(z)$ gives the probable distribution of transitions during the time of the collision.

Table 3.3-3

Shape Factors Associated with $P_{i j \to k l}^{class\ (t)}$ for a Straight Line

Trajectory

$z = \dfrac{gt}{b}$ *	$S(z)$	$S'(z)$
0.00	0.500	0.000
0.05	0.504	0.173
0.10	0.517	0.335
0.15	0.537	0.475
0.20	0.564	0.587
0.25	0.596	0.666
0.30	0.630	0.712
0.40	0.703	0.718
0.50	0.771	0.641
0.60	0.830	0.526
0.70	0.876	0.407
0.80	0.911	0.302
0.90	0.937	0.218
1.00	0.956	0.155
1.10	0.969	0.109
1.20	0.978	0.076
1.30	0.984	0.053
1.40	0.989	0.037
1.50	0.992	0.026
1.60	0.994	0.018
1.70	0.996	0.013
1.80	0.997	0.009
1.90	0.998	0.007
2.00	0.998	0.005

* Values of $S(z)$ and $S'(z)$ for negative z may be obtained

by the relations $S(-z) = 1 - S(z)$ and $S'(-z) = S(+z)$.
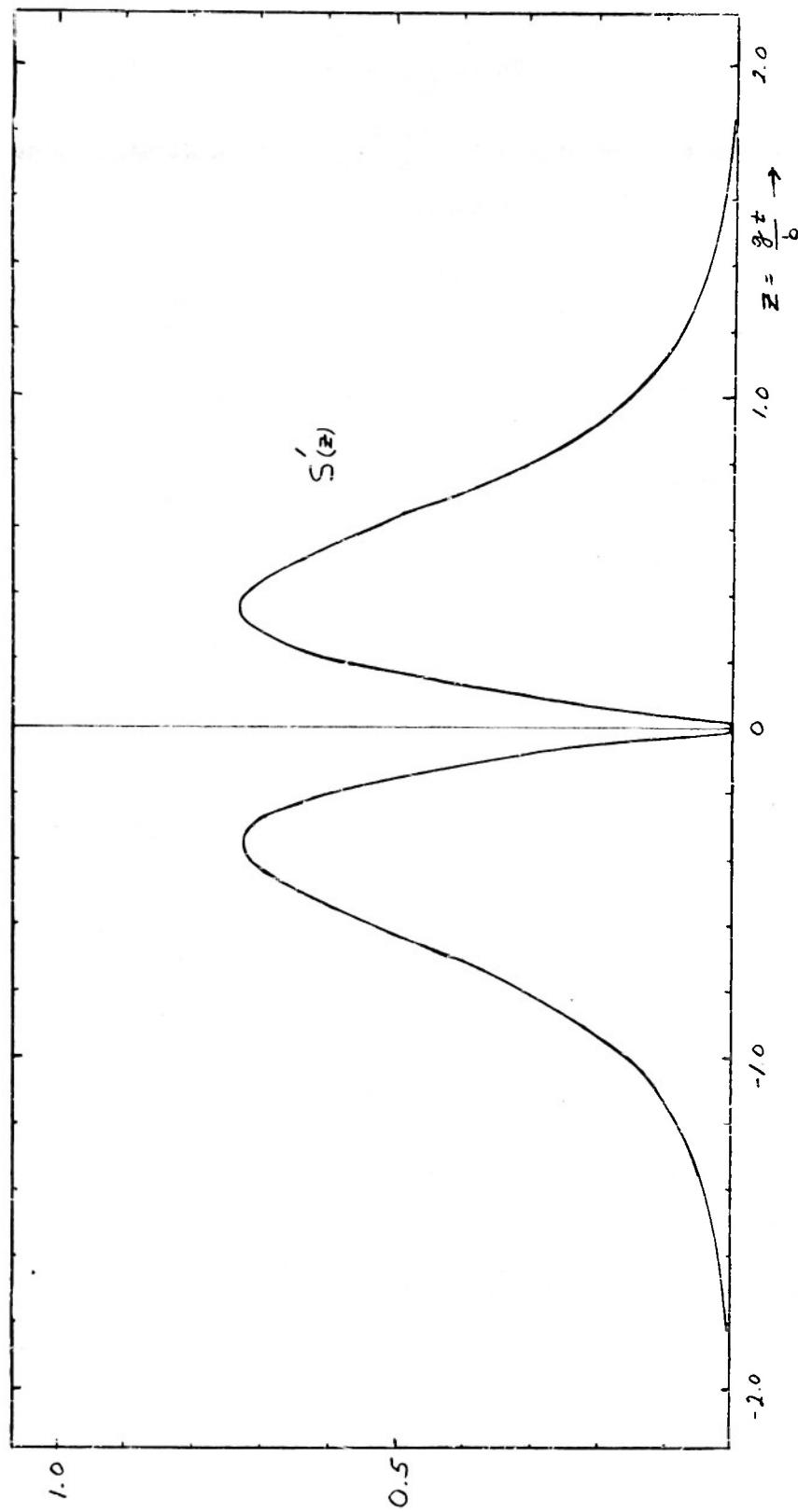
Fig. 3.3-4 The shape factor S'(z), where $z = \frac{gt}{b}$. The probability that a transition occurs between time t and t + dt along a straight line constant velocity trajectory is $S'(z) \frac{g}{b} P^{(1)}_{i \to x t} dt$.

some cases, as in head on collisions, the particles may spend a long
time in the configuration of closest approach and the probability of
transition in this region may not be small. This may be seen by writing
$\frac{d}{dt}\left[P_{i_i \to k_i}^{(i)}(t)\right]$ as a function of the arc length s. Then

$$\frac{d}{ds}\left[P_{i_i \to k_i}^{(i)}(s)\right] = \frac{(\psi_{mi}^{k\ell}|\frac{d\Phi}{ds}|\psi_{mi}^{i})}{\Delta E_{ij}^{k\ell}(t(s))} 2\Re_e\left[e^{-\frac{i}{\hbar}\int_{-\infty}^{t(s)}\Delta E_{ij}^{k\ell}(\theta)d\theta}\int_{-\infty}^{s}\frac{e^{+\frac{i}{\hbar}\int_{-\infty}^{t(s)}\Delta E_{ij}^{k\ell}(\theta)d\theta}}{\Delta E_{ij}^{k\ell}(s)}(\psi_{mi}^{k\ell}|\frac{d\Phi}{ds}|\psi_{mi}^{i})ds\right] \quad (3.3-7)$$

Now in trajectories which are nearly like the straight line constant
velocity paths used in this section, $\frac{d\Phi}{ds}$ is indeed zero at the distance
of closest approach, so that the probability of a transition occurring
in the element of trajectory ds about the distance of closest approach
is indeed zero, as pictured in Fig. 3.3-4. In a head-on collision,
however, the arc length s becomes identical with the intermolecular
distance R_{ab}, and the function $\frac{d\Phi}{ds}$ is now large in the vicinity of the
distance of closest approach. (Actually it is not defined just at the
distance of closest approach because of a cusp in the function
at that point, but on both sides of the cusp $\frac{d\Phi}{ds}$ will in general be
large.) Thus in the limit of a head on collision, the probability of a
transition in the element ds about the distance of closest approach may
become large. It is interesting to note that in the limit of b = 0, a
head-on collision, the two maxima of Fig. 3.3-4 move toward the
origin, indicating the likelihood of a transition in this region.

The trajectory along which we are carrying out the time dependent
perturbation calculation is symmetric, about t = 0, so in some sense
it is true that the average location of the transition in grazing collisions
is at the distance of closest approach. In kinetic theory applications,
however, we are interested in the angle of deflection resulting from
the transition, so that it is by no means valid to expect that the
distance of closest approach would be an appropriate average location

for all transitions.

d) The transition probability for resonant collisions

The considerations of the probability of transition thus far in this section have been limited to non resonance interactions, since we have assumed that $\triangle E_{ij}^{\kappa \ell} \neq 0$ in all of our formulae and calculations. The classical analogue of a quantum mechanical system in resonance[15] pictures the extra quantum of energy as being transferred rapidly back and forth between the colliding molecules, so that in a measurement of the system there is equal probability of finding either molecule in the higher energy state.

That this resonance situation applies to collisions in which the collision parameter b is so large that there is no appreciable deflection of the trajectory is indicated by the theoretical interpretation of the observed pressure broadening of microwave spectra. Experimental values of the collision cross sections for the self broadening of spectral lines of polar molecules give collision diameters which are three to four times larger than the kinetic theory collision diameters. That is, whereas most kinetic theory diameters are in the range of three to five Ångstroms, the microwave diameters usually lie in the range of ten to twenty Ångstroms.

The theory of pressure broadening[16] indicates that the largest contribution to the cross section for polar molecules comes from resonant collisions, and that the observed microwave collision diameters may be interpreted approximately as the critical value of the collision parameter b for which the probability of transition

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15. D. Bohm, loc. cit.,p. 477.
16. For a summary of the microwave theroy and experimental data, and a guide to the literature, see W. Gordy, W. Smith and R. Trambarulo, Microwave Spectroscopy, Wiley, 1953, p. 188.

during the encounter is one half.

Thus, for collisions in which the collision parameter is less than the microwave value of the collision diameter, we are justified in considering both final states of the system as equally likely. For collision parameters larger than this value, the angle of deflection in most encounters is negligible.

APPENDIX I

ALMOST ADIABATIC TIME DEPENDENT PERTURBATIONS[*]

When the Hamiltonian of a system changes slowly with the time, we may expect to be able to approximate solutions of Schroedinger's equation by means of stationary state energy eigenfunctions of the instantaneous Hamiltonian.

Let the Hamiltonian of a system be $H(x, t)$, where t is the time, and x denotes all of the space coordinates. Let $v(x, \theta)$ be the stationary state solutions obtained by setting $t = \theta$, a constant. The $v_n(x, \theta)$ are given by

$$H(x, \theta)\, v_n(x, \theta) = E_n(\theta)\, v_n(x, \theta) \tag{A-1}$$

We assume that the $v_n(x, \theta)$ form a complete orthonormal set of functions in the space coordinates at every time.

If the total wave function of the system is known at zero time, we may at later times write

$$\Psi(x, t) = \sum_j A_j(t)\, v_j(x, t)\, e^{-\frac{i}{\hbar}\int_0^t E_j(\theta)\, d\theta} \tag{A-2}$$

The expansion coefficients $A_j(t)$ depend on time, and the form of the exponential time factor has been chosen for convenience in subsequent differentiations.

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[*] The following derivation is essentially the same as those found in D. Bohm, loc. cit., p. 497, and L. I. Schiff, loc. cit., p. 207.

We may obtain the expansion coefficients $A_j(t)$ by requiring that $\Psi(x,t)$ satisfy the second Schroedinger equation

$$H \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \tag{A-3}$$

This gives

$$0 = i\hbar \sum_j \left[\dot{A}_j(t) \, v_j(x,t) + A_j(t) \, \dot{v}_j(x,t) \right] e^{-\frac{i}{\hbar} \int_0^t E_j(\theta) \, d\theta} \tag{A-4}$$

Multiplying by $v_m^*(x, t) \, e^{\frac{i}{\hbar} \int_0^t E_m(\theta) \, d\theta}$ and integrating over all x, we obtain

$$0 = \dot{A}_m(t) + \sum_j A_j(t) \, (v_m | \dot{v}_j) \, e^{-\frac{i}{\hbar} \int_0^t \left[E_j(\theta) - E_m(\theta) \right] d\theta} \tag{A-5}$$

where we have used the orthonormal properties of the $v_j(x, t)$.

This result may be simplified by rewriting the matrix elements $(v_m | v_j)$. From Eq. A-1

$$H v_j = E_j v_j$$

Differentiating with respect to the time, we obtain

$$\dot{H} v_j + H \dot{v}_j = \dot{E}_j v_j + E_j \dot{v}_j \tag{A-6}$$

If we multiply by $v_m^*(m \neq j)$, and integrate over all x, we get immediately,

$$(v_m | \dot{H} | v_j) + (v_m | H | \dot{v}_j) = E_j (v_m | \dot{v}_j) \tag{A-7}$$

Since H is Hermetian,

$$(v_m | H | \dot{v}_j) = E_m (v_m | \dot{v}_j)$$

Thus Eq. A-7 gives

$$(v_m \mid \dot{v}_j) = \frac{(v_m \mid \dot{H} \mid v_j)}{E_j - E_m} \qquad (A-8)$$

and Eq. A-5 may be written

$$\dot{A}_m(t) = \sum_{j \neq m} A_j(t) \frac{(v_m \mid \dot{H} \mid v_j)}{E_m - E_j} e^{-\frac{i}{\hbar} \int_0^t (E_j - E_m) d\theta} + A_m(t)(v_m \mid \dot{v}_m) \quad (A-9)$$

From here we proceed as in the usual method of the variation of constants. If we assume that at $t = -\infty$ the system was in the pure state v_0, we may approximate the $A_j(t)$ as

$$A_j(t) = \delta_{jo}$$

so that

$$\dot{A}_m(t) = \frac{e^{-\frac{i}{\hbar} \int_{-\infty}^t [E_0(\theta) - E_m(\theta)] d\theta}}{E_0(\theta) - E_m(\theta)} (v_m \mid \dot{H} \mid v_0) \qquad (A-10)$$

The probability that at time t the system will be found in the m'th state is now

$$P_{0 \to m}^{(t)} = \left| \int_{-\infty}^t \frac{e^{-\frac{i}{\hbar} \int_{-\infty}^{t'} [E_0(\theta) - E_m(\theta)] d\theta}}{E_0(t) - E_m(t)} (v_m \mid \dot{H} \mid v_0) \, dt' \right|^2 \qquad (A-11)$$

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